

VISIT...

LANZAROTE
Caliente.COM

LITHIUM OXIDE

[12057-24-8]

Formula: Li_2O ; MW 29.88

Synonym: lithium monoxide

Uses

Lithium oxide in its highly porous sintered form is used as an absorbent for carbon dioxide.

Physical Properties

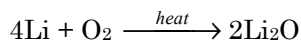
White cubic crystals; refractive index 1.644; density 2.013 g/cm³; melts at 1,570°C; dissolves and decomposes in water (6.67 g/100g at 0°C and 10.02 g/100g at 100°C).

Thermochemical Properties

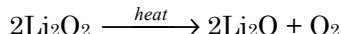
ΔH_f° (cry)	-142.91 kcal/mol
ΔH_f° (gas)	-38.4 kcal/mol
ΔG_f° (cry)	-134.13 kcal/mol
ΔG_f° (gas)	-43.3 kcal/mol
S° (cry)	8.98 cal/degree mol
S° (gas)	55.30 cal/degree mol
C_p (cry)	12.93 cal/degree mol
C_p (gas)	11.91 cal/degree mol

Preparation

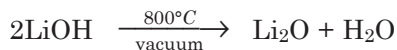
Lithium oxide is prepared by heating lithium metal in dry oxygen above 100°C:



Another method of preparation that yields pure lithium oxide involves thermal decomposition of lithium peroxide:

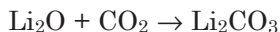


Also, the oxide can be produced by heating the pure lithium hydroxide at 800°C in a vacuum:



Reactions

Lithium oxide absorbs carbon dioxide forming lithium carbonate:



The oxide reacts slowly with water forming lithium hydroxide:



There is no reaction with oxygen at high temperature or high pressure to form any peroxide or higher oxide.

The oxide reacts with acids forming lithium salts.

Analysis

Elemental composition: Li 46.45%, O 53.55%. The oxide may be identified from its physical properties and characterized by x-ray analysis. Lithium composition in the oxide may be determined by analyzing the nitric acid extract by AA or ICP (See Lithium).

LITHIUM SULFATE

[10377-48-7]

Formula: Li_2SO_4 ; MW 109.94

Also forms a stable monohydrate, $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ [10102-25-7]

Uses

Lithium sulfate is used in making a special type of high strength glass. It also is used in medicine as an antidepressant.

Physical Properties

Colorless monoclinic or hexagonal crystals; transforms to cubic form at 500°C; refractive index 1.465; density 2.221 g/cm³; sublimes at 845°C; soluble in water, solubility decreases with an increase in temperature (26.1 and 23.2 g at 0 and 100°C, respectively); insoluble in absolute ethanol and acetone.

The monohydrate constitutes colorless monoclinic crystals; refractive index 1.465; density 2.06 g/cm³; loses water of crystallization at 130°C; soluble in water, (more soluble than the anhydrous salt (34.9 and 29.2 g/100g at 25 and 100°C), respectively; insoluble in acetone and pyridine.

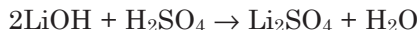
Thermochemical Properties

ΔH_f° (Li_2SO_4)	-343.33 kcal/mol
ΔH_f° ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$)	-414.80 kcal/mol
ΔH_f° (Li SO_4)(aq)	-350.44 kcal/mol
ΔG_f° (Li_2SO_4)	-315.91 kcal/mol
ΔG_f° ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$)	-374.2 kcal/mol
ΔG_f° (Li SO_4)(aq)	-318.18 kcal/mol
S° (Li_2SO_4)	27.5 cal/degree mol
S° ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$)	39.1 cal/degree mol
S° (Li SO_4)(aq)	11.3 cal/degree mol

C_p (Li_2SO_4)	28.10 cal/degree mol
C_p ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$)	36.1 cal/degree mol

Preparation

Lithium sulfate is prepared by neutralization of lithium hydroxide or lithium carbonate with sulfuric acid followed by crystallization:



The product obtained from crystallization in a concentrated solution is the monohydrate, $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. Anhydrous salt is obtained by heating the monohydrate in a vacuum.

Analysis

Elemental composition (anhydrous Li_2SO_4): Li 12.63%, S 29.12%, O 59.28%. The waters of crystallization may be determined by gravimetry. Lithium may be analyzed in a dilute aqueous solution by AA or ICP (See Lithium), while sulfate may be measured by ion chromatography.

LUTETIUM

[7439-94-3]

Symbol Lu; atomic number 71; atomic weight 174.97; a lanthanide series element; an *f*-block inner-transition metal; electron configuration $[\text{Xe}]4f^{14}5d^16s^2$; valence +3; atomic radius (coordination number 12) 1.7349Å; ionic radius (Lu^{3+}) 0.85Å; two naturally-occurring isotopes: Lu-176 (97.1%) and Lu-175(2.59%); Lu-172 is radioactive with a half-life of 4×10^{10} years (beta-emission); several artificial isotopes known, that have mass numbers 155, 156, 167–174, 177–180.

History, Occurrence, and Uses

Lutetium was independently discovered by Urbain and von Welsbach in 1907. The element was named after Lutetia, the ancient name for Paris. The metal also is known as cassiopeium in Germany.

Lutetium occurs in nature in small amounts in yttrium-containing minerals. It is found in xenotime, precambrian granites, and North American shales. It also exists at 0.001% in monazite, from which the metal is produced commercially. Lutetium has very little commercial application. The metal emits beta particles after thermal neutron activation, and is used to catalyze organic reactions.

Physical Properties

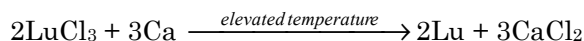
Silvery-white metal; hexagonal close-packed structure; density 9.84 g/cm³; melts at 1,663°C; vaporizes at 3,402°C; electrical resistivity 59 microhm-cm; slightly paramagnetic; thermal neutron cross section 108 barns; soluble in acids.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	102.2 kcal/mol
ΔG_f° (gas)	96.7 kcal/mol
S° (cry)	12.18 cal/degree mol
S° (gas)	44.14 cal/degree mol
C_p (cry)	6.42 cal/degree mol
C_p (gas)	4.99 cal/degree mol
ΔH_{fus} (cry)	4.60 kcal/mol
ΔH_{vap} (cry)	102.2 kcal/mol\

Production

Lutetium is produced commercially from monazite. The metal is recovered as a by-product during large-scale extraction of other heavy rare earths (See Cerium, Erbium, Holmium). The pure metal is obtained by reduction of lutetium chloride or lutetium fluoride by an alkali or alkaline earth metal at elevated temperatures;

**Chemical Properties**

In aqueous media lutetium occurs as tripositive Lu^{3+} ion. All its compounds are in +3 valence state. Aqueous solutions of all its salts are colorless, while in dry form they are white crystalline solids. The soluble salts such as chloride, bromide, iodide, nitrate, sulfate and acetate form hydrates upon crystallization. The oxide, hydroxide, fluoride, carbonate, phosphate, and oxalate of the metal are insoluble in water. The metal dissolves in acids forming the corresponding salts upon evaporation of the solution and crystallization.

Analysis

The metal may be analyzed by AA, ICP-AES, ICP/MS, x-ray fluorescence and other instrumental techniques.

MAGNESIUM

[7439-95-4]

Symbol Mg; atomic number 12; atomic weight 24.305; a Group II A (Group 2) alkaline-earth metal; atomic radius 1.60Å; ionic radius (Mg^{2+}) 0.72Å; atomic volume 14.0 cm³/mol; electron configuration $[\text{Ne}]3s^2$; valence +2; ionization potential 7.646 and 15.035eV for Mg^+ and Mg^{2+} , respectively; three natural isotopes: Mg-24(78.99%), Mg-25(10.00%), Mg-26(11.01%).

History, Occurrence and Uses

Magnesium was discovered by Davy in 1808. He produced an amalgam of magnesium both by chemical and electrolytic methods. Metallic mercury was

used in both methods. In the chemical method, Davy passed potassium vapors over magnesia at red heat and extracted the 'new element' with mercury. In the electrolytic reduction, magnesium sulfate was electrolyzed using a mercury cathode. Both the methods yielded the amalgam of the new element. Magnesium in the metallic form was first isolated by French chemist Bussy in 1828 by heating magnesium chloride with potassium metal at elevated temperatures. Faraday in 1833 produced metallic magnesium by electrolysis of magnesium chloride.

Magnesium is probably one of the most common metals distributed in nature, constituting about 2.4% of the earth's crust. The metal, however, does not occur in nature in elemental form. The principal minerals are dolomite $[\text{CaMg}(\text{CO}_3)_2]$, magnesite MgCO_3 ; carnallite $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, and silicate materials, such as talc $\text{Mg}_3(\text{Si}_4\text{O}_{10})(\text{OH})_2$ and asbestos $\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_9$. Magnesium also is found in seawater, natural underground brines and salt deposits. Its concentration in sea water is 1,350 mg/L. Magnesium also occurs in all plants. Its porphyrin complex, chlorophyll, is essential for photosynthesis. It also is an essential nutrient element for humans. The dietary requirement for adults is about 300 mg per day.

Magnesium metal and its alloys have numerous uses in chemical, electrochemical, metallurgy, and electronic industries. Its thermal and electrical properties, lightness, and ease of fabrication into useful shapes make it an attractive choice in industrial applications. The metal is alloyed with aluminum for various structural uses. Its alloys with zinc, copper, nickel, lead, zirconium and other metals have many uses too. Magnesium alloys are used in automobile parts, aircraft, missiles, space vehicles, ship hulls, underground pipelines, memory discs, machine tools, furniture, lawn mowers, ladders, toys, and sporting goods. It also is used in making small and lightweight dry cell batteries. Chemical applications of magnesium include its use as a reducing agent, to prepare Grignard reagent for organic syntheses, and to purify gases. Magnesium also is used in blasting compositions, explosive sensitizers, incendiaries, signal flares, and pyrotechnics. Magnesium salts have numerous uses. They are discussed individually.

Physical Properties

Silvery-white metal; close-packed hexagonal structure; density 1.74 g/cm³ at 20°C, 1.57 g/cm³ at 650°C (liquid melt); melts at 650°C; vaporizes at 1,090°C; vapor pressure 5 torr at 678°C and 20 torr at 763°C; electrical resistivity 4.46 microhm-cm at 20°C, 28.0 microhm-cm at 650°C (liquid melt); surface tension 563 dynes/cm at 681°C; modulus of elasticity 6.5×10^6 lb/sq in; Poisson's ratio 0.35; thermal neutron absorption cross section 0.059 barn; soluble in dilute acids.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	35.16 kcal/mol
ΔG_f° (gas)	26.89 kcal/mol
S° (cry)	7.82 cal/degree mol

S° (gas)	35.52 cal/degree mol
C_p (cry)	5.95 cal/degree mol
C_p (gas)	4.97 cal/degree mol
ΔH_{fus}	2.03 kcal/mol
ΔH_{vap}	49.9 kcal/mol
Thermal conductivity at 27°C	1.56 W/cm. K
Coefficeint of linear expansion (20–100°C)	$26.1 \times 10^{-6}/^\circ\text{C}$

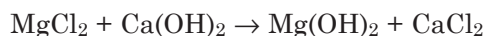
Production

Although many commercial processes have been developed since the first electrolytic isolation of Mg metal by Davy and Faraday, and Bussy, by chemical reduction, the principles of the manufacturing processes have not changed. At present, the metal is most commonly manufactured by electrolytic reduction of molten magnesium chloride, in which chlorine is produced as a by-product. In chemical reduction processes, the metal is obtained by reduction of magnesium oxide, hydroxide, or chloride at elevated temperatures.

All the magnesium produced in the world currently is derived from its minerals dolomite and carnallite, as well as from the underground brines and seawaters. In most processes, magnesium is recovered from its mineral or brine either as magnesium chloride or converted to the latter for electrolytic production.

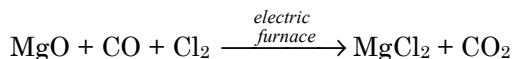
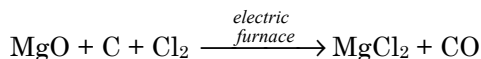
Many subterranean brines are very rich in magnesium chloride, often containing about 11% MgCl_2 . Sodium and calcium chlorides are the other two major components (c.12% NaCl and 2% CaCl_2) in such brines. Solar evaporation of the brine solution and repeated heating increases the MgCl_2 concentration in the brine to above 25% at which the solubility of NaCl significantly decreases and it can be filtered out. Repeated spray drying and purification by chlorination yields anhydrous magnesium chloride.

Magnesium chloride produced from dolomite for electrolysis involves a series of steps that include calcinations of the mineral to oxide and then conversion to magnesium hydroxide, neutralization of the hydroxide with hydrochloric acid to form hydrated chloride, addition of sulfuric acid to separate out calcium as its insoluble sulfate, and dehydration of the hydrated salt to yield anhydrous MgCl_2 . Similar steps are also followed to obtain the metal from seawater. The average concentration of magnesium ion in seawater is about 1,200 mg/L, thus making ocean water an enormous source of magnesium. Magnesium is precipitated as hydroxide by treatment with lime in an agitated flocculator:

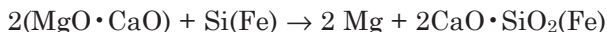


The insoluble Mg(OH)_2 is filtered off and the seawater containing calcium chloride is returned to the sea. The hydroxide is then neutralized with hydrochloric acid. Evaporation of the solution yields hexahydrate, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. The hexahydrate is either fully dehydrated to anhydrous MgCl_2 by heating in dryers or partially dehydrated to monohydrate for electrolytic

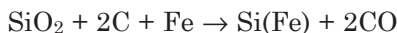
production of metal. Magnesium hydroxide produced from seawater alternatively may be calcined to magnesium oxide, MgO . The latter is reduced with carbon and converted to magnesium chloride by heating in an electric furnace in the presence of chlorine gas:



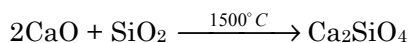
Manufacturing processes, based on thermal reduction of magnesium oxide employ ferrosilicon or carbon as a reducing agent and use dolomite as the starting material. In these processes, the mineral is first calcined to produce oxides of magnesium and calcium, $\text{MgO} \cdot \text{CaO}$. In one such batch process, known as the Pidgeon process, calcined dolomite is mixed with pulverized ferrosilicon powder, briquetted, and charged into an electrically-heated retort made of nickel-chrome-steel alloy and operated under vacuum (0.1 to 0.2 mm Hg). The reaction is carried out at about $1,150^\circ\text{C}$ for several hours (8 hours). Silicon reduces magnesium oxide to metallic magnesium produced as vapor. The vapors condense into crystals in the cooler zone of the retort (500°C). The reactions are as follows:



The ferrosilicon alloy required in the above process is produced by thermal reduction of silica with carbon in the presence of iron:

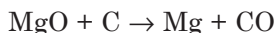


In the Pidgeon process discussed above, a secondary side reaction occurs between the CaO and SiO_2 forming dicalcium silicate:



In a modified method known as Magnetherm process, sufficient aluminum oxide is added to melt this Ca_2SiO_4 slag. This allows the products to be removed in the molten state and, in addition, heats the reactor by the electrical resistance of the slag.

Magnesium also is produced by thermal reduction of its oxide by carbon:

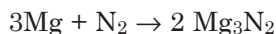
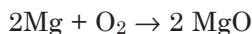


The above reaction is reversible above $1,850^\circ\text{C}$. The metal produced as vapor must be cooled rapidly to prevent any reversible reactions. Rapid cooling (shock cooling) can quench the reaction giving finely divided pyrophoric dust

of the metal. The separation, however, is difficult. This makes the carbon reduction process less attractive than the other two thermal reduction processes, namely Pidgeon and Magnetherm processes.

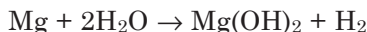
Reactions

At room temperature magnesium is not attacked by air. However, when heated it burns with a dazzling white light, forming the oxide, MgO and nitride, Mg_3N_2 . The formation of oxide is an exothermic reaction. The heat of reaction causes a portion of the metal to combine with the nitrogen of air:



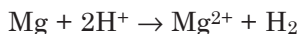
When the metal is in a finely divided state or a thin foil, both the reactions above are rapid.

Magnesium reacts very slowly with water at ordinary temperatures. Although the metal occupies a position higher than hydrogen in the electrochemical series, the reaction practically stops after a thin protective film of insoluble hydroxide deposits over the surface of the metal. The reaction is moderately fast in hot water and rapid in steam. The products are magnesium hydroxide and hydrogen:



In the presence of ammonium chloride or a substance that dissolves $\text{Mg}(\text{OH})_2$, the above reaction proceeds at ambient temperatures, the metal continues to dissolve in water, displacing hydrogen.

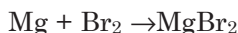
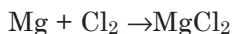
Magnesium reacts readily with most mineral acids, evolving hydrogen:



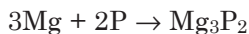
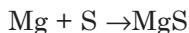
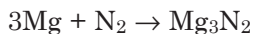
However, with certain acids, such as hydrofluoric acid, a protective layer of insoluble magnesium fluoride terminates the reaction. Likewise, the metal has little action on chromic acid.

At ordinary temperatures magnesium is stable in alkalies, both dilute and concentrated. However, hot solutions of alkalies above 60°C attack the metal.

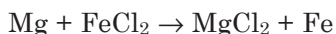
Magnesium combines with halogens at elevated temperatures forming halides:



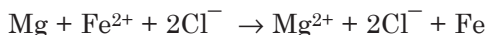
The metal reacts with nitrogen, phosphorus, sulfur and selenium at elevated temperatures forming their binary compounds:



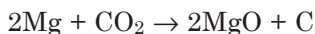
Magnesium exhibits single displacement reactions, thus replacing lower metals in electrochemical series from their salt solutions or melt. For example, magnesium will replace iron from molten iron(II) chloride forming magnesium chloride:



Or it will reduce Fe^{2+} to metallic iron from the aqueous solution of FeCl_2 :



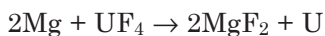
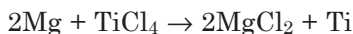
Magnesium also reduces nonmetallic oxides, such as carbon dioxide, carbon monoxide, sulfur dioxide and nitrous oxide, burning at elevated temperatures.



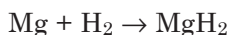
The metal reduces ammonia to magnesium nitride:



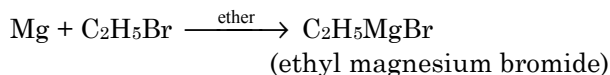
Two important reduction reactions of magnesium that are of commercial interest are the production of titanium by Kroll process and obtaining uranium from its fluoride:



Magnesium forms hydride when heated with hydrogen under pressure:



Probably the most important reaction of magnesium in terms of synthetic applications involves preparation of Grignard reagent, RMgX where R is an alkyl or aryl group and X is a halogen other than fluorine. Grignard reagents provide convenient routes for various organic syntheses. These reagents are made by the reaction of magnesium with an alkyl or aryl halide in ether:



Analysis

Magnesium in trace amounts can be measured conveniently in aqueous and solid matrices by flame atomic absorption or by ICP emission spectroscopy. The sample is digested with nitric acid and diluted. The recommended wavelength for flame AA measurement is 285.2nm and for ICP/AES analysis 279.08 or 279.55 nm. The metal also can be measured by the gravimetric method in which diammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$ is added to an ammoniacal solution of magnesium or its compound to produce a yellow precipitate of magnesium ammonium phosphate which on ignition yields magnesium pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7$. The solid or aqueous sample is digested with nitric acid and then hydrochloric acid, evaporated and diluted prior to adding $(\text{NH}_4)_2\text{HPO}_4$ and ammonia solution. The method is less sensitive than the AA or ICP techniques and also subject to interference from calcium, aluminum, iron, silica and ammonium chloride.

MAGNESIUM ACETATE

[142-72-3]

Formula: $\text{Mg}(\text{OOCCH}_3)_2$; MW 142.39; also exists as stable tetrahydrate, $\text{Mg}(\text{OOCCH}_3)_2 \cdot 4\text{H}_2\text{O}$ [16674-78-5] and monohydrate $\text{Mg}(\text{OOCCH}_3)_2 \cdot \text{H}_2\text{O}$ [60582-92-5].

Uses

Magnesium acetate is used in the manufacture of rayon fiber for cigarette filters; and as a fixative for dyes in textile printing. It also is used as an anti-septic and disinfectant.

Physical Properties

Anhydrous magnesium sulfate is a white crystalline solid occurring in alpha form as orthorhombic crystals or as a beta form having triclinic structure; density 1.507 and 1.502 g/cm³ for alpha- and beta-forms, respectively; decomposes at 323°C; very soluble in water; moderately soluble in methanol (5.25g/100 mL at 15°C).

The tetrahydrate constitutes colorless monoclinic crystals; hygroscopic; density 1.454 g/cm³; melts at 80°C; highly soluble in water (120 g/100mL at 15°C); very soluble in methanol and ethanol.

Preparation

Magnesium acetate is prepared by treating magnesium oxide with acetic acid. Magnesium oxide reacts with concentrated acetic acid in boiling ethyl acetate to produce the alpha form of anhydrous magnesium acetate. The beta form is obtained by treating the oxide with 5–6% acetic acid. In slightly hydrated isobutyl alcohol medium the product is a monohydrate, $\text{Mg}(\text{OOCCH}_3)_2 \cdot \text{H}_2\text{O}$. In aqueous solution magnesium acetate crystallizes as a tetrahydrate, the commercial product. The tetrahydrate dehydrates to anhy-

drous salt at 134°C.

Analysis

Elemental composition for anhydrous acetate: Mg 17.08%, C 33.73%, H 4.25%, O 44.74%. The water of crystallization in the commercial product can be measured by gravimetry. Acetate anion can be estimated from elemental analysis for C, H and O, or by ion chromatography in a very dilute aqueous solution. Mg can be determined by AA or ICP methods.

MAGNESIUM BROMIDE

[7789-48-2]

Formula: MgBr_2 ; MW 184.11; forms stable hexahydrate, $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ [13446-53-2] and decahydrate, $\text{MgBr}_2 \cdot 10\text{H}_2\text{O}$ [75198-45-7].

Occurrence and Uses

Magnesium bromide occurs in sea water, surface and subterranean brines, and salt deposits. It is an electrolyte component in certain dry cells. In medicine, it is a sedative and anticonvulsant for treatment of nervous disorder. It also is used in organic synthesis forming several addition compounds.

Physical Properties

The anhydrous MgBr_2 is a white crystalline substance; hexagonal crystals; deliquescent; density 3.72 g/cm³; melts at 700°C; highly soluble in water (101.5g/100mL at 20°C); moderately soluble in methanol and ethanol (21.8 and 6.9 g/mL at 20°C, respectively).

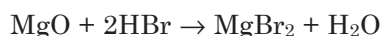
The hexahydrate, $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ consists of colorless monoclinic crystals; bitter taste; hygroscopic; fluoresce in x-rays; density 2.07 g/cm³; melts at 172.4°C; intensely soluble in water, 316 g/100 mL at 0°C; dissolves in methanol and ethanol; slightly soluble in ammonia solution.

Thermochemical Properties

ΔH_f° (cry)	-125.3 kcal/mol
ΔH_f° (gas)	-74.0 kcal/mol
ΔH_f° (aq)	-169.7 kcal/mol
ΔG_f° (cry)	-120.4 kcal/mol
S° (cry)	28.0 cal/degree mol

Preparation

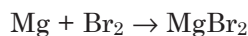
Magnesium bromide is prepared by treating magnesium oxide with hydrobromic acid and subsequent crystallization above 0°C. The product is hexahydrate, $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$:



The anhydrous MgBr_2 may be obtained by heating the hexahydrate with

dry hydrogen bromide gas.

Magnesium bromide also can be made from its elements. Heating magnesium metal with bromine vapor yields the salt:



Magnesium bromide, like the chloride salt, is obtained from sea water (see Magnesium and Magnesium chloride). In this process, magnesium hydroxide precipitated from sea water is neutralized with hydrobromic acid, and MgBr_2 is obtained by crystallization.

Analysis

Elemental composition: Mg 13.20%, Br 86.80%. The aqueous solution is analyzed for Mg by AA or ICP technique and the bromide ion measured by ion chromatography.

MAGNESIUM CARBONATE

[13717-00-5]

Formula: MgCO_3 ; MW 84.31; several hydrated and basic carbonates are also known that are stable and occur in nature. The types, names, formulas and CAS Registry numbers of anhydrous, hydrated and basic magnesium carbonates are tabulated below:

Compound	Mineral	Formula	CAS No.
anhydrous salt	magnesite	MgCO_3	[13717-00-5]
dihydrate	barringtonite	$\text{MgCO}_3 \cdot 2\text{H}_2\text{O}$	[5145-48-2]
trihydrate	nesquehonite	$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$	[14457-83-1]
pentahydrate	lansfordite	$\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$	[61042-72-6]
basic carbonate	artinite	$\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$	[12143-96-3]
basic carbonate	hydromagnesite	$4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$	[12072-90-1]
basic carbonate	dypingite	$4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$	[12544-02-4]
basic carbonate	—	$4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	[75300-49-1]

Occurrence and Uses

Magnesium carbonate occurs in nature in several minerals as hydrated, basic and double salts, as shown above. The two principal minerals are magnesite, MgCO_3 and dolomite, a double salt, $\text{CaCO}_3 \cdot \text{MgCO}_3$. Both minerals are used as source materials in the production of magnesium metal. Also, they are calcined to produce basic refractory bricks. Other applications of magnesium carbonate are in flooring, fireproofing and fire-extinguishing compositions; as a filler material and smoke suppressant in plastics; as a reinforcing agent in neoprene rubber; as a drying agent and for color retention in foods; in cos-

metics; in dusting powder; and in toothpaste. The high purity magnesium carbonate is used as an antacid in medicine; and as an additive to table salt. Another important application of magnesium carbonate is as a starting material in producing a number of magnesium compounds.

Physical Properties

The anhydrous salt consists of white trigonal crystals; refractive index 1.717; density 2.958 g/cm³; decomposes at 350°C; practically insoluble in water (106 mg/L at room temperature); K_{sp} 1.0×10^{-5} ; low to moderate solubility under partial pressure of CO₂ (3.5 and 5.9 g MgCO₃/100g saturated solution at CO₂ pressure 2 and 10 atm, respectively); insoluble in acetone and ammonia; dissolves in acids.

The di- and trihydrates, MgCO₃·2H₂O and MgCO₃·3H₂O are colorless crystals having triclinic and monoclinic structures, respectively; the refractive index 1.458 and 1.412, respectively; and their densities are 2.825 and 1.837 g/cm³. The pentahydrate, MgCO₃·5H₂O, occurring naturally as the mineral lansfordite is a white crystalline solid; monoclinic crystals; refractive index 1.456; density 1.73g/cm³; decomposes in air; slightly soluble in water (0.375 g/100 mL at 20°C).

All three basic carbonates, artinite, hydromagnesite and dypingite, are white crystalline substances of monoclinic crystal structures; refractive index 1.488, 1.523 and 1.508, respectively; the index of refraction for the basic carbonate octahydrate is 1.515; the densities are 2.02 and 2.16 g/cm³ for artinite and hydromagnesite; the basic carbonates are all practically insoluble in water.

Thermochemical Properties

ΔH_f° (MgCO ₃)	−261.9 kcal/mol
ΔG_f° (MgCO ₃)	−241.9 kcal/mol
ΔG_f° (MgCO ₃ ·3H ₂ O)	−412.6 kcal/mol
ΔG_f° (MgCO ₃ ·5H ₂ O)	−525.7 kcal/mol
S° (MgCO ₃)	15.7 cal/degree mol
C_p (MgCO ₃)	18.05 cal/degree mol

Preparation

Magnesium carbonate is obtained mainly by mining its natural mineral magnesite. The trihydrate salt, MgCO₃·3H₂O, is prepared by mixing solutions of magnesium and carbonate ions in the presence of carbon dioxide. Alternatively, it may be produced by carbonation of a magnesium hydroxide slurry with carbon dioxide under pressure (3.5 to 5 atm) and at a temperature below 50°C which yields soluble magnesium bicarbonate:



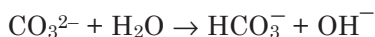
The solution is filtered to remove impurities and the filtrate is subjected to vacuum or aeration to yield insoluble magnesium carbonate as a hydrated salt:



Under ordinary conditions, anhydrous magnesium carbonate cannot be prepared in aqueous systems. The anhydrous salt, however, can be made under very high partial pressures of carbon dioxide.

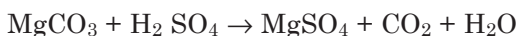
Basic magnesium carbonate occurs in nature as the mineral hydromagnesite. The basic salt is obtained by mining the ore followed by purification. The basic carbonates also can be made by drying the magnesium carbonate trihydrate at about 100°C. Alternatively it can be prepared by simply boiling a solution of magnesium bicarbonate. The bicarbonate is obtained by carbonation of a magnesium hydroxide slurry below 50°C and under a CO₂ partial pressure of 3.5 to 5 atm. Composition of the basic carbonate produced by the above methods is 4MgCO₃ · Mg(OH)₂ · 4H₂O.

Another basic salt, MgCO₃ · Mg(OH)₂ · 3H₂O is precipitated when magnesium salt solution is treated with sodium carbonate solution. The reactions probably are:



Reactions

Magnesium carbonate dissolves in dilute mineral acids, evolving carbon dioxide:

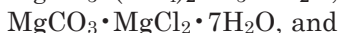
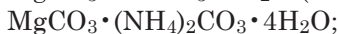
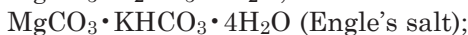


Thermal dissociation at elevated temperatures yields magnesium oxide and CO₂:



The trihydrate, MgCO₃ · 3H₂O or other hydrates on heating form basic magnesium carbonates, the product compositions depending on degree of water of crystallization and temperature.

Magnesium carbonate forms several double salts with salts of alkali and alkaline earth metals and ammonium ion. Some examples are:



Analysis

Elemental composition: Mg 28.83%, C 14.24%, O 56.93%. A measured

amount of magnesium carbonate is treated with dilute HCl and liberated CO_2 is identified by the limewater test (CO_2 turns limewater milky). Carbon dioxide also may be identified and quantified by GC-TCD or preferably by GC/MS (characteristic mass ion 44). The acid solution can be analyzed for magnesium by AA or ICP techniques.

MAGNESIUM CHLORIDE

[7786-30-3]

Formula: MgCl_2 ; MW 95.218; also occurs as hexahydrate, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ [13778-96-6].

Occurrence and Uses

Magnesium chloride is a constituent of sea water. It also is found in most natural brines and many minerals such as carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot \text{H}_2\text{O}$. Its hexahydrate occurs in nature as mineral bischofite, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.

The most important use of magnesium chloride is in the electrolytic production of magnesium metal. The compound is also used to make oxychloride cement, or what is known as Sorel cement for flooring, fire-resistant panel, and fireproofing of steel beams and other materials. Other applications are: as a dust binder on roads; as a flocculating agent in water treatment; for dressing cotton and woolen fabrics; as a fire-extinguishing agent and a fireproofing material; in processing of sugar-beets; and as a catalyst.

Physical Properties

Anhydrous salt consists of white lustrous hexagonal crystals; refractive index 1.675; density 2.32 g/cm^3 ; melts at 714°C ; decomposes at a lower temperature of 300°C when heated slowly, releasing chlorine; vaporizes at $1,412^\circ\text{C}$; highly soluble in water, releasing heat (solubility 54.2 g/100 mL at 20°C and 72.7 g/100mL at 100°C) moderately soluble in ethanol (7.4 g/100mL at 30°C).

Hexahydrate constitutes colorless monoclinic crystals; deliquescent; refractive index 1.495; density 1.569 g/cm^3 ; decomposes on heating at 116°C ; highly soluble in water (157 g/100mL at 20°C); solubility increased on heating; soluble in alcohol.

Thermochemical Properties

ΔH_f° (MgCl_2)	-153.28 kcal/mol
ΔH_f° ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$)	-597.28 kcal/mol
ΔG_f° (MgCl_2)	-141.45 kcal/mol
ΔG_f° ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$)	-505.49 kcal/mol
S° (MgCl_2)	21.42 cal/degree mol
S° ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$)	87.50 cal/degree mol
C_p (MgCl_2)	17.06 cal/degree mol
C_p ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$)	75.30 cal/degree mol

Production

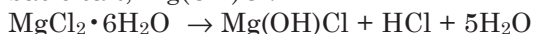
Magnesium chloride is prepared by treating magnesium carbonate, hydroxide or oxide with hydrochloric acid followed by crystallization by evaporation. The hexahydrate of the salt $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ is obtained upon crystallization.

In most commercial processes, the compound is either derived from the sea water or from the natural brines, both of which are rich sources of magnesium chloride. In the sea water process, the water is treated with lime or calcined dolomite (dolime), $\text{CaO} \cdot \text{MgO}$ or caustic soda to precipitate magnesium hydroxide. The latter is then neutralized with hydrochloric acid. Excess calcium is separated by treatment with sulfuric acid to yield insoluble calcium sulfate. When produced from underground brine, brine is first filtered to remove insoluble materials. The filtrate is then partially evaporated by solar radiation to enhance the concentration of MgCl_2 . Sodium chloride and other salts in the brine concentrate are removed by fractional crystallization.

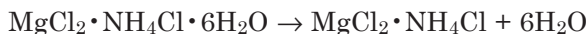
The crude product containing magnesium oxide or hydroxide is purified by heating with chlorine.

Magnesium chloride can be also recovered from its mineral carnallite by similar processes involving concentration of the liquor by solar evaporation followed by separation of other salts by fractional crystallization.

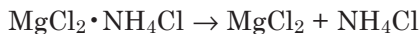
The product obtained is always the hexahydrate, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. It is dehydrated to anhydrous magnesium chloride by spray drying and heating with dry hydrogen chloride gas. In the absence of HCl , heating hexahydrate yields the basic salt, $\text{Mg}(\text{OH})\text{Cl}$:



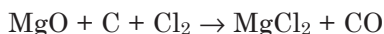
Pure anhydrous chloride can be prepared by heating the double salt $\text{MgCl}_2 \cdot \text{NH}_4\text{Cl} \cdot 6\text{H}_2\text{O}$:



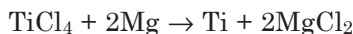
Ammonium chloride sublimes on further heating, leaving pure anhydrous MgCl_2 :



Other methods of preparation involve heating magnesium oxide with coke powder in the presence of chlorine:



Magnesium chloride also is a by-product during reduction of titanium(IV) chloride with magnesium metal:



The anhydrous salt and the hexahydrate are both highly corrosive. They are handled in equipment made out of inconel.

Analysis

Elemental composition (anhydrous MgCl_2): Mg 25.54%, Cl 74.46%. Aqueous solution of the salt may be analyzed for Mg by AA or ICP method (See Magnesium). The chloride ion can be identified by ion chromatography or measured by titration with a standard solution of silver nitrate using potassium chromate as indicator.

MAGNESIUM FLUORIDE

[7783-40-6]

Formula: MgF_2 ; MW 62.31

Synonym: magnesium flux

Occurrence and Uses

Magnesium fluoride occurs in nature as the mineral, sellaite. It is used in glass and ceramics. Single crystals are used for polarizing prisms and lenses.

Physical Properties

Colorless tetragonal crystals; faint violet luminescence; refractive index 1.378; density 3.148 g/cm^3 ; Moh's hardness 6; melts at 1261°C ; vaporizes at $2,260^\circ\text{C}$; practically insoluble in water (76 mg/L at 18°C); soluble in nitric acid; slightly soluble in dilute acids and acetone; insoluble in ethanol.

Thermochemical Properties

ΔH_f°	-268.5 kcal/mol
ΔG_f°	-255.8 kcal/mol
S°	$13.68 \text{ cal/degree mol}$
C_p	$14.72 \text{ cal/degree mol}$

Preparation

Magnesium fluoride is prepared by treating a magnesium salt solution with hydrofluoric acid or sodium fluoride:



or by adding hydrofluoric acid to magnesium carbonate:

**Analysis**

Elemental composition: Mg 39.02%, F 60.98%. The compound is digested with nitric acid-hydrofluoric acid mixture, diluted and analyzed for magnesium by AA or ICP method. The crystals may be characterized nondestructively by x-ray crystallography.

MAGNESIUM HYDRIDE

[60616-74-2]

Formula: MgH_2 ; MW 26.321**Uses**

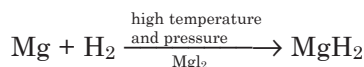
Magnesium hydride is a reducing agent; a source of hydrogen; and serves to prepare many complex hydrides.

Physical Properties

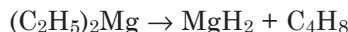
White tetragonal crystals; rutile structure; density 1.45 g/cm³; decomposes at 200°C; reacts with water.

Preparation

Magnesium hydride is obtained by combining the elements at about 500°C. A convenient method of preparation involves passing hydrogen under pressure over heated magnesium powder in the presence of magnesium iodide as catalyst.



Magnesium hydride also is produced by thermal decomposition of diethylmagnesium at 200°C:

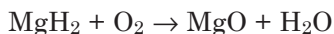


An active form of the hydride obtained as a solvated pyrophoric powder and used as a reducing agent is prepared by the reaction of dibutylmagnesium $(\text{C}_4\text{H}_9)_2\text{Mg}$ with phenylsilane, $\text{C}_6\text{H}_5\text{SiH}_3$ in ether-heptane solvent mixture.

Reactions

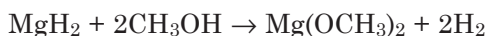
Magnesium hydride is not readily decomposed by heat. However, in high vacuum decomposition takes place at 280°C, the hydride dissociating to its elements.

Magnesium hydride is a strong reducing agent, reducing oxidizable substances and compounds containing oxygen. The reactions often progress with violence. It ignites spontaneously in air, forming magnesium oxide and water:

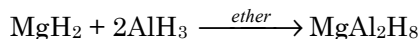
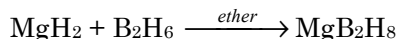


It reacts violently with water, evolving hydrogen.

Similar reaction occurs with methane forming magnesium methoxide and evolving hydrogen:



Magnesium hydride forms double hydrides with aluminum hydride and boron hydride:



Analysis

Elemental composition: Mg 92.35%, H 7.65%. The compound may be identified from its chemical properties that involve the evolution of hydrogen when cautiously treated with water or methanol (See Hydrogen). Magnesium may be analyzed by various instrumental techniques after digesting the compound into aqueous phase aided by nitric acid.

Hazard

Flammable solid, ignites spontaneously in air. Reaction with water is violent with the evolution of hydrogen.

MAGNESIUM HYDROXIDE

[1309-42-8]

Formula: $\text{Mg}(\text{OH})_2$; MW 58.327

Synonym: brucite

Occurrence and Uses

Magnesium hydroxide occurs in nature as mineral brucite, often associated with several other minerals such as calcite, magnesite, or talc. Magnesium hydroxide is used as an intermediate in making magnesium metal. It also is used to manufacture magnesium oxide, magnesium carbonate and several other magnesium salts. Milk of magnesia, a finely divided suspension of magnesium hydroxide in water, is used in medicine as a laxative and antacid.

Physical Properties

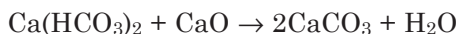
Colorless hexagonal plate; refractive index 1.559; density 2.36 g/cm³; loses water at 350°C; practically insoluble in water (9mg/L at 18°C and 40 mg/L at 100°C); soluble in acids and in aqueous solutions containing NH_4^+ ion.

Thermochemical Properties

ΔH_f°	−220.97 kcal/mol
ΔG_f°	−199.23 kcal/mol
S°	15.10 cal/degree mol
C_p	18.41 cal/degree mol

Production

Magnesium hydroxide is commonly produced from seawater, which is rich in Mg^{2+} ion. The average concentration of Mg^{2+} in seawater is about 1,300 mg/L. The first step of the process involves removal of interfering substances from seawater, the most notable being the water-soluble calcium bicarbonate. Bicarbonate removal is crucial, as it can form insoluble calcium carbonate, a side product that cannot be separated from magnesium hydroxide readily. Acidification of seawater converts bicarbonate into carbon dioxide, which is degassed by heating. Alternatively, seawater is treated with lime to convert calcium bicarbonate to carbonate:



Lime is obtained by calcination of dolomite, $\text{CaCO}_3 \cdot \text{MgCO}_3$, or limestone, CaCO_3 , under controlled conditions to remove all CO_2 . After bicarbonate removal, the seawater is then treated with calcium hydroxide, slaked dolime or sodium hydroxide to precipitate magnesium hydroxide:



The solution is seeded with magnesium hydroxide to enhance crystal growth.

Magnesium hydroxide also is obtained from waste liquors from the potash industry. It is precipitated from mother liquors containing magnesium salts.

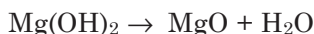
In the laboratory, magnesium hydroxide may be prepared by double decomposition reactions by adding a soluble hydroxide to solutions of magnesium salts; i.e., adding caustic soda solution to magnesium sulfate solution:



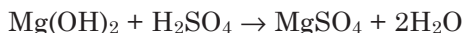
The above precipitation reaction does not occur with ammonium hydroxide in the presence of excess ammonium chloride.

Reactions

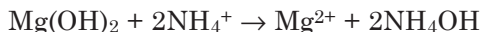
Solid magnesium hydroxide is decomposed by heat, forming magnesium oxide:



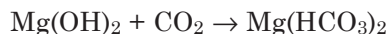
Magnesium hydroxide is a weak base. However, it is sufficiently strong to neutralize acids, forming their salts. For example, treatment with sulfuric acid followed by evaporation and crystallization yields magnesium sulfate:



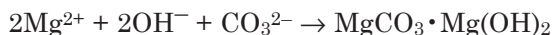
Magnesium hydroxide is soluble in solutions containing excess ammonium ion:



Carbonation of its slurry with carbon dioxide at 4 to 5 atm pressure yields magnesium bicarbonate:



Treatment with sodium carbonate solution yields basic carbonate. The probable reaction step is as follows:



Similarly, basic magnesium chloride of indefinite composition is produced when magnesium hydroxide is mixed with magnesium chloride and water. The product is used as oxychloride cement (see Magnesium Oxide).

MAGNESIUM IODIDE

[10377-58-9]

Formula: MgI_2 ; MW 278.12; forms two stable hydrates, hexahydrate $\text{MgI}_2 \cdot 6\text{H}_2\text{O}$ [75535-11-4] and octahydrate $\text{MgI}_2 \cdot 8\text{H}_2\text{O}$ [7790-31-0].

Uses

Magnesium iodide has few commercial applications. The salt is used to prepare several addition compounds with organic solvents, some of which are used in organic synthesis.

Physical Properties

The anhydrous iodide is white hexagonal solid; deliquescent; density 4.43 g/cm³; decomposes at 637°C; highly soluble in water (148 g/100mL at 18°C); soluble in alcohol, ether and ammonia.

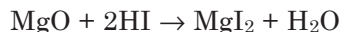
The octahydrate is white orthorhombic crystals; deliquescent; density 2.098 g/cm³; decomposes at 41°C; very soluble in water (81g/100 mL at 20°C); soluble in alcohol and ether.

Thermochemical Properties

ΔH_f°	-87.0 kcal/mol
ΔG_f°	-85.6 kcal/mol
S°	31.0 cal/degree mol

Preparation

Magnesium iodide is prepared by the reaction of magnesium oxide, hydroxide or carbonate with hydriodic acid, followed by evaporation of the solution and crystallization:





Analysis

Elemental composition (anhydrous MgI_2): Mg 8.72%, I 91.26%. Aqueous solution may be analyzed for Mg by AA or ICP, and for iodide by ion chromatography following appropriate dilution.

MAGNESIUM NITRATE

[10377-60-3]

Formula: $\text{Mg}(\text{NO}_3)_2$; MW 148.31; forms two stable hydrates; the hexahydrate $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ [13446-18-9] and the dihydrate, $\text{Mg}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ [15750-45-5].

Occurrence and Uses

The hexahydrate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, occurs in nature as mineral nitromagnesite. Magnesium nitrate is used in pyrotechnics; and in the manufacture of concentrated nitric acid to remove water and concentrate the acid vapors to 90–95% HNO_3 . It also is used to aid coating and prilling in production of ammonium nitrate. The salt also is used as an analytical standard for magnesium and a matrix modifier in furnace atomic absorption spectroscopic analysis. It also finds some limited application as a nitrogenous fertilizer.

Physical Properties

The anhydrous salt consists of white cubic crystals; density 2.3 g/cm^3 ; very soluble in water. The dihydrate is white crystalline solid having density 1.45 g/cm^3 ; decomposes at about 100°C ; soluble in water and ethanol. The hexahydrate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is a colorless solid having monoclinic crystal structure and density 1.46 g/cm^3 . The salt is hygroscopic and very soluble in water and moderately soluble in ethanol.

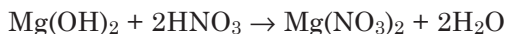
Thermochemical Properties

ΔH_f°	−189.0 kcal/mol
ΔG_f°	−147.4 kcal/mol
S°	39.2 cal/degree mol
C_p	33.9 cal/degree mol

Preparation

Magnesium nitrate is prepared by the action of nitric acid on magnesium carbonate, oxide or hydroxide:





The salt crystallizing at room temperature after evaporation is the hexahydrate, $\text{Mg(NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

Reactions

Thermal decomposition of anhydrous $\text{Mg(NO}_3)_2$ yields magnesium oxide and nitrogen oxides. Heating the hexahydrate above its melting point forms basic nitrates, such as $\text{Mg(NO}_3)_2 \cdot 4\text{Mg(OH)}_2$. The latter decomposes at 400°C , forming magnesium oxide and oxides of nitrogen. Magnesium nitrate forms addition compounds with a number of nitrogen-containing organics such as pyridine, aniline, and urea.

Analysis

Elemental composition (anhydrous $\text{Mg(NO}_3)_2$); Mg 16.39%, N 18.88%, O 64.73%. The water of crystallization can be measured by gravimetry. Magnesium content of the salt can be measured by analysis of the metal in an aqueous solution using AA or ICP. Nitrate anion can be measured by ion chromatography—or by using a nitrate ion-selective electrode.

MAGNESIUM OXIDE

[1309-48-4]

Formula: MgO ; MW 40.30

Synonym: magnesite; magnesite usta

Uses

Magnesium oxide occurs in nature as the mineral periclase. The commercial product is manufactured in several grades, depending on the purity, particle size and the reactivity desired. Dead-burned magnesite (consisting of sintered micro-crystals) is used in production of basic refractory brick for cement kilns, furnaces and crucibles. The caustic-burned magnesite, more reactive than the dead-burned reactive grade, is used to manufacture various magnesium salts; in extraction of uranium oxide from uranium ore; as mineral supplement in animal feed; and in many catalytic applications. Caustic-burned magnesite of higher reactive-grade, available as light or heavy magnesite, is used in cosmetics as fillers; as an accelerator for vulcanization of rubber; as an ingredient of antacids; and to prepare magnesium metal and various metal salts. Fused magnesite in crushed form is used in electrical arc furnaces and domestic appliances as insulation.

Physical Properties

Periclase: Colorless, transparent cubic crystals or white very-fine powder; refractive index 1.736; density 3.58 g/cm^3 ; hardness 5.5 Mohs; melts at

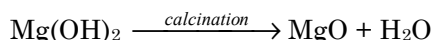
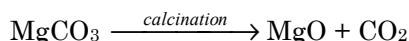
2,852°C; vaporizes at 3,600°C; electrical resistivity 1.3×10^{15} ohm-cm at 27°C; practically insoluble in water (86 mg/L at 30°C); soluble in acids and ammonium salt solutions; insoluble in alcohol.

Thermochemical Properties

ΔH_f°	-143.81 kcal/mol
ΔG_f°	-136.10 kcal/mol
S°	6.44 cal/degree mol
C_p	8.88 cal/degree mol
Thermal conductivity at 27°C	60.0 W/m.K

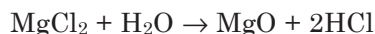
Production

Magnesium oxide is produced either from its minerals or from seawater or brine. Among minerals, magnesite, MgCO_3 and dolomite, $\text{MgCO}_3 \cdot \text{CaCO}_3$ are the two primary sources. It also may be obtained from its hydroxide ore, brucite, $\text{Mg}(\text{OH})_2$. Calcination of these minerals yields magnesium oxide. The minerals generally contain several impurities, such as silica, alumina, iron oxide, and oxides and silicates of calcium and other metals. The ore is crushed, sized and impurities are separated by various processes, including froth flotation, magnetic separation, dissolution, and a wide-range of chemical process depending on the chemical properties of impurities. Often magnesium ore is converted into one of its salts, such as carbonate, hydroxide, chloride, or sulfate by chemical processes. The salt on calcination yields magnesium oxide:



If dolomite is the source, thermal decomposition of MgCO_3 at 350°C produces MgO . At this temperature, CaCO_3 does not decompose. The decomposition temperature for the latter is 850°C.

Magnesium oxide also is produced from sea water and subterranean brine. Magnesium ion is precipitated as hydroxide by treating seawater with calcium or sodium hydroxide following a series of concentration steps (See magnesium). The hydroxide is then calcined to yield oxide. If brine is the source, it is concentrated, purified and calcined:



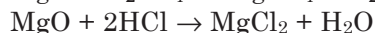
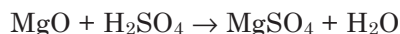
Calcination temperature is very important in the production process and dictates the particle size, purity and reactivity of the product. A dead-burned, sintered dense microcrystalline product is obtained at calcination temperature of 1,400 to 1,700°C. A caustic-burned product is obtained when magnesium carbonate or hydroxide is calcined at 600 to 700°C. A light grade (specific gravity 2.9) highly reactive caustic-burned magnesia that contains some moisture and carbon dioxide is obtained at about 600°C. A denser form from

heavy caustic-burned oxide is produced when the carbonate or hydroxide is calcined at 800 to 900°C.

Magnesium oxide also can be prepared by heating magnesium metal in oxygen.

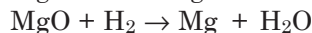
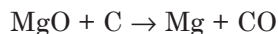
Reactions

Unlike calcium oxide, at ordinary temperatures magnesium oxide is stable in water. There is very little formation of magnesium hydroxide. The reaction, however, is rapid at elevated temperatures. The acids form their magnesium salts which, if water-soluble, may be obtained by evaporation of the solution:



Heating the oxide with carbon dioxide yields magnesium carbonate, MgCO_3 .

The oxide can be reduced to metallic magnesium by heating with a reducing agent such as carbon or hydrogen at elevated temperatures:



Analysis

Elemental composition: Mg 60.32%, O 39.68%. The oxide can be identified nondestructively by x-ray methods. Oxygen content may be determined by elemental microanalysis. Magnesium may be analyzed by AA or ICP following dissolution of the oxide in nitric acid and appropriate dilution with water.

MAGNESIUM PERCHLORATE

[10034-81-8]

Formula: $\text{Mg}(\text{ClO}_4)_2$; MW 223.21; forms several hydrates including a stable hexahydrate, $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$

Synonyms: Anhydron; Dehydrite

Uses

Magnesium perchlorate is a drying agent for gases; and also an oxidizing agent.

Physical Properties

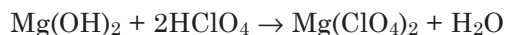
White granular or flaky powder; highly deliquescent; density 2.21 g/cm³; decomposes at 251°C; very soluble in water (99.3g/100mL at 18°C); soluble in ethanol (24g/100mL) at 25°C.

Hexahydrate constitutes white rhombohedral crystals; refractive index

1.482; density 1.98 g/cm³; melts around 185°C; very soluble in water, releasing heat.

Preparation

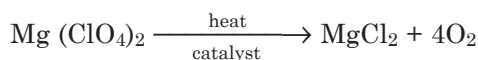
Magnesium perchlorate may be prepared by adding perchloric acid to an aqueous solution of magnesium hydroxide. Crystallization yields hexahydrate, $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$.



Reactions

Magnesium perchlorate is a strong oxidizing agent. In aqueous solutions and in acid medium the most conspicuous reactions are those involving oxidation—characteristic of the oxidizing action of perchlorate ion, ClO_4^- .

Thermal decomposition in the presence of a catalyst, such as manganese dioxide, yields magnesium chloride and oxygen:



Analysis

Elemental composition (for anhydrous salt): Mg 10.89%, Cl 31.77%, O 57.34%. In the aqueous solution of the compound, Mg is analyzed by AA or ICP and perchlorate ion by ion chromatography or by redox titration. Also the solid salt may be mixed with MnO_2 and heated. Oxygen liberated may be tested by flaming of a glowing splinter, and the MgCl_2 residue may be dissolved in water, filtered, and the aqueous solution may be analyzed for Cl^- by titration or ion chromatography and Mg determined by AA or ICP (See Magnesium Chloride).

MAGNESIUM PHOSPHATES, BASIC

Magnesium phosphate forms three basic salts, as follows:

(i) Monobasic salt: $\text{MgH}_4(\text{PO}_4)_2$; MW 218.28; CAS No. [13092-66-5]

Synonyms: magnesium biphosphate; primary magnesium phosphate; acid magnesium phosphate; magnesium tetrahydrogen phosphate

(ii) Dibasic salt: MgHPO_4 ; MW 120.29; CAS No. [7757-86-0]; also forms a stable trihydrate, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$; the trihydrate is found in nature as the minerals, newberyite and phosphoroeslerite.

Synonyms: magnesium hydrogen phosphate; secondary magnesium phosphate

(iii) Tribasic salt: $\text{Mg}_3(\text{PO}_4)_2$; MW 262.86; CAS No. [7757-87-1]; forms stable hydrates $\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, and $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$; the octahydrate occurs naturally as the mineral bobierite.

Synonyms: magnesium orthophosphate, neutral magnesium phosphate, tri-

magnesium phosphate

Uses

All basic magnesium phosphates find applications in plastics as stabilizers. Other than this, monobasic salt is used in fireproofing wood. The dibasic phosphate is a food additive; and also a laxative. The tribasic phosphate is an antacid; and a nutritional food supplement. The compound also is an adsorbent; and a polishing agent in dental work.

Physical Properties

The monobasic phosphate as dihydrate is a white crystalline powdery material; hygroscopic; decomposes on heating; dissolves in water; soluble in acids with reaction; insoluble in alcohol.

The dibasic magnesium phosphate trihydrate is a white crystalline powder; orthorhombic structure; refractive index 1.514; density 2.123 g/cm³ at 15°C; melts at 205°C losing a molecule of water; decomposes between 550 to 650°C; slightly soluble in water; soluble in acid; insoluble in ethanol. The heptahydrate $\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$ constitutes white monoclinic needles; density 1.728 g/cm³ at 15°C; sparingly soluble in water (3g/L at 20°C); soluble in acids; insoluble in ethanol.

The tetrahydrate of the tribasic phosphate, $\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ is a bulky and soft white powdery material; monoclinic crystals; density 1.64 g/cm³ at 15°C; slightly soluble in water (0.2 g/L at 20°C); soluble in acids. The naturally occurring octahydrate, bobierite, is a white crystalline solid, containing monoclinic plates; refractive index 1.510; density 2.195 g/cm³ at 15°C; loses three molecules of water of crystallization at 150°C; loses all water at 400°C; insoluble in water; soluble in dilute mineral acids.

Magnesium orthophosphate $\text{Mg}_3(\text{PO}_4)_2$ constitutes rhombic crystals; melts at 1,184°C; insoluble in water; soluble in ammonium salt solution.

Thermochemical Properties [$\text{Mg}_3(\text{PO}_4)_2$]

ΔH_f°	−903.6 kcal/mol
ΔG_f°	−845.8 kcal/mol
S°	45.2 cal/degree mol
C_p	51.0 cal/degree mol

Preparation

The basic phosphates that occur naturally may be mined from their respective minerals. They may be prepared by reactions of phosphoric acid with magnesium oxide and hydroxide followed by crystallization. Monobasic and dibasic magnesium phosphate are prepared by the action of phosphoric acid on magnesium hydroxide and magnesium oxide, respectively. The tribasic phosphate is made by treating magnesium oxide with phosphoric acid at high temperature.

Analysis

Basic magnesium phosphates may be characterized by x-ray and thermogravimetric analyses and elemental analysis. Magnesium may be determined

by AA or ICP after digestion in nitric acid followed by dilution. Alternatively, the compounds can be analyzed for magnesium nondestructively, but with lesser sensitivity, using x-ray fluorescence. The phosphorus content may be measured by dissolving the basic phosphate in sulfuric acid, diluting the acid extract and treating the diluted acid solution with ammonium molybdate-ammonium metavanadate reagent, and measuring the intensity of the yellow color formed using a spectrophotometer at 400 to 490 nm wavelength. Alternatively, the acid solution may be treated with ammonium molybdate and stannous chloride reagent to produce an intense blue color that may be measured at 690 or 650 nm. The concentration may be determined from a phosphate standard calibration curve (APHA, AWWA, and WEF, 1999. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. Washington D.C.: American Public Health Association.)

MAGNESIUM SILICATES

Magnesium forms an array of silicates having varying structures. Such a wide variety of silicates include metasilicate, orthosilicate, pyrosilicate, polysilicates, and a number of complex silicates, such as asbestos and talc in combination with other metal ions. Many such silicates occur in nature either as complex silicates or as discrete magnesium silicate. Some important magnesium silicates are listed below:

(i) Magnesium metasilicate: MgSiO_3 [13776-74-4]; MW 100.39; occurs in nature as minerals enstatite, clinoenstatite, and protoenstatite. It has pyroxene-type structure consisting of $(\text{SiO}_3^{2-})_n$ chain. The metasilicate consists of white monoclinic crystals having density 3.19 g/cm³. The compound decomposes at 1550°C.

(ii) Magnesium orthosilicate: Mg_2SiO_4 [26686-77-1]; MW 140.69; occurs in nature as the mineral forsterite. It is a white crystalline solid consisting of orthorhombic crystals. It has a density 3.21 g/cm³ and melts at 1,898°C.

(iii) Magnesium trisilicate: $\text{Mg}_2\text{Si}_3\text{O}_8$; also known as magnesium mesotrisilicate; occurs in nature as minerals sepiolite, parasepiolite, and meerschaum. The compound is obtained as a fine white powder. Its pentahydrate occurs in nature as the mineral sellagen.

(iv) Chrysotile [12001-29-5], a white serpentine fibrous silicate, is a major asbestos mineral. It is a tetrasilicate compound of magnesium, having the formula $\text{Mg}_6\text{Si}_4\text{O}_{10}(\text{OH})_8$ containing $(\text{Si}_4\text{O}_{11}^{6-})_n$ chain.

(v) Complex silicates: magnesium silicate is a component of several complex silicates, including tremolite, an amphibole-type tetrasilicate $\text{Ca}_2\text{Mg}_5(\text{Si}_4\text{O}_{11})_2$ containing double-strand cross-linked $(\text{Si}_4\text{O}_{11}^{6-})_n$; and diopside, a calcium magnesium metasilicate $[\text{CaMg}(\text{SiO}_3)_2]$ consisting of pyroxene-type single-strand chains of composition $(\text{Si}_4\text{O}_3^{2-})_n$.

(vi) Talc [14807-96-6] or talcum: a very finely powdered hydrous magnesium silicate. Its formula is $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_2$ or $3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{HOH}$. It occurs in nature in compact and lump form, known as steatite or soapstone. The latter

is an impure variety of steatite. Talc is a white or grayish-white powder, density 2.7 g/cm^3 and adheres readily to skin.

Magnesium silicates have numerous applications in several industries, such as ceramics, glass, refractories, paints, rubber, chemicals, and food. Some general applications include manufacture of dry resins and resinous compositions; filler for rubber, paper and soap; bleaching agent for vegetable oils; anticaking agent in food; catalyst; pigment in paints and varnishes; dusting and shoe powder; toilet preparations; heat and electric insulators; and antacid and gastric sedative in medicine and a filler for pills. Florisil, a porous and granular form of activated magnesium silicate, is used for cleanup of sample extracts from interfering substances in gas chromatographic analysis.

Thermochemical Properties (Mg_2SiO_4)

ΔH_f°	-519.6 kcal/mol
ΔG_f°	-491.2 kcal/mol
S°	22.7 cal/degree mol
C_p	28.3 cal/degree mol

Production

Magnesium silicate occurs in nature in a variety of minerals, and is mined. The pyrosilicate is prepared by treating an aqueous solution of a magnesium salt with a solution of sodium silicate. The active form can be made by adjusting drying temperature and degree of hydration.

Analysis

Magnesium silicates are characterized by x-ray diffraction and Raman spectroscopy. Magnesium is analyzed in an aqueous acid extract by AA or ICP following digestion of the solid with nitric acid and appropriate dilution.

MAGNESIUM SULFATE

[7487-88-9]

Formula: MgSO_4 ; MW 120.36. Forms several stable hydrates, many of which occur in nature. The hydrates, their formulas, mineral names, and CAS Registry Numbers are tabulated below:

Hydrate	Mineral Name	Formula	CAS No.
monohydrate	kieserite	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$	[14168-73-1]
tetrahydrate	starkeyite	$\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$	[24378-31-2]
pentahydrate	pentahydrate	$\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$	[15553-21-6]
hexahydrate	hexahydrate	$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$	[13778-97-7]
heptahydrate	epsomite	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	[10034-99-8]

Occurrence and Uses

Magnesium sulfate is found in nature in many salt deposits and mineral waters, occurring as hydrates or double salts. The heptahydrate or Epsom salt

was discovered in 1695, found in the mineral water at Epsom. Kieserite and epsomite are the two most important minerals. Other than these and the above hydrates, magnesium sulfate also is found in several other minerals, including:

langbeinite,	$\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$	[13826-56-7]
leonite	$\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$	[15226-80-9]
vanthoffite	$3\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4$	[15557-33-2]
bloedite	$\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$	[15083-77-9]
kainite	$4\text{KCl} \cdot 4\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$	[67145-93-1]
polyhalite	$\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	[15278-29-2].

Magnesium sulfate is used widely in several industries including fertilizer, cement, textile, chemicals, and medicine. In the cement industry, it is used in manufacturing oxysulfate cement. In medicine, it is an analgesic and cathartic. An important application of anhydrous magnesium sulfate in the laboratory involves drying organic solvents required for syntheses and GC analysis.

In the textile industry, magnesium sulfate is used in finishing composition for dressing cotton; for weighting and sizing silk; as a mordant for fixing basic dyestuffs on wool; and in fireproofing fabrics. It also is a component of certain types of electrolytic plating baths; of various photographic solutions; of cosmetic lotions. It is a catalyst carrier; a dietary supplement in cattle feed; a coagulant for rubber and plastic; and is used in making citric acid and several magnesium salts, such as magnesium stearate.

Physical Properties

The anhydrous salt consists of colorless rhombohedral crystals; density 2.66 g/cm³; decomposes at 1,124°C; dissolves in water (269 g/100mL at 0°C), ethanol and glycerol; sparingly soluble in ether (1.16 g/mL at 18°C); insoluble in acetone.

The monohydrate $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, as the mineral kieserite, consists of colorless monoclinic crystals; refractive index 1.523; density 2.445 g/cm³; becomes anhydrous on heating at 200°C; soluble in water.

Epsom salt, or heptahydrate $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, constitutes colorless monoclinic or rhombohedral crystals; refractive index 1.433; density 1.68 g/cm³; loses six molecules of water of crystallization at 150°C and converts to anhydrous form at 200°C; highly soluble in water (71 g/100mL at 20°C); slightly soluble in alcohol and glycerol.

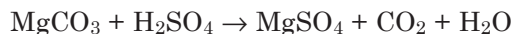
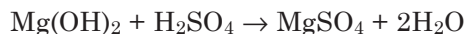
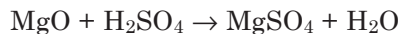
Thermochemical properties

ΔH_f° (MgSO_4)	−307.1 kcal/mol
ΔH_f° ($\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$)	−453.2 kcal/mol
ΔH_f° ($\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$)	−596.7 kcal/mol
ΔH_f° ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$)	−737.8 kcal/mol
ΔH_f° ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$)	−809.9 kcal/mol
ΔG_f° (MgSO_4)	−279.8 kcal/mol
ΔG_f° ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$)	−629.1 kcal/mol

ΔG_f° ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$)	−686.4 kcal/mol
S° (MgSO_4)	21.9 cal/degree mol
S° ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$)	83.2 cal/degree mol
S° ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$)	89.0 cal/degree mol
C_p (MgSO_4)	23.0 cal/degree mol
C_p ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$)	83.2 cal/degree mol

Production

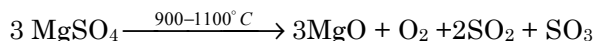
Hydrated magnesium sulfate occurs in nature as the minerals kieserite and epsomite. The salt is mined in large scale from these and other naturally occurring minerals. The salt also is prepared in the laboratory by the action of sulfuric acid on magnesium oxide, hydroxide, or carbonate followed by evaporation and crystallization:



Crystallization at temperatures between 1.8 and 48°C yields heptahydrate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. Below 1.8°C, a dodecahydrate, $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$ crystallizes out. Above 48°C crystals of lower hydrates form. The anhydrous salt is obtained by heating the heptahydrate at about 500°C in a rotary drum; or dehydrating above 150°C in the presence of sulfuric acid.

Reactions

The anhydrous salt decomposes at elevated temperatures to magnesium oxide, oxygen, sulfur dioxide, and sulfur trioxide. The decomposition commences around 900°C and is complete at about 1,100°C. The overall reaction is:



On the other hand, heating hydrated sulfate above 150°C yields magnesium oxysulfate, a hydrolysis reaction. No dehydration or thermal decomposition occurs.

The anhydrous salt may be reduced to magnesium oxide when heated with carbon at 750°C:



Magnesium sulfate undergoes three important types of reactions in aqueous solutions: double decomposition, double salt formation, and formation of oxysulfate cements. Many insoluble magnesium salts may be precipitated out by double decomposition reactions:



Magnesium sulfate forms several double salts having varying stoichiometric compositions. When gaseous ammonia is bubbled through magnesium sulfate solution, several hydrated double salts are obtained by crystallization.

Magnesium sulfate double salts have the compositions $\text{MgSO}_4 \cdot \text{NH}_3 \cdot 3\text{H}_2\text{O}$; $\text{MgSO}_4 \cdot 2\text{NH}_3 \cdot 4\text{H}_2\text{O}$; and $\text{MgSO}_4 \cdot 2\text{NH}_3 \cdot 2\text{H}_2\text{O}$ (Copp, A. N. 1981. *Magnesium Compounds*, In Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Vol. 14, pp. 636-40, New York: Wiley Interscience.) Similarly, in sulfuric acid, crystals of double salts $\text{MgSO}_4 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot \text{H}_2\text{SO}_4$, and $\text{MgSO}_4 \cdot 3\text{H}_2\text{SO}_4$ are obtained.

Addition of magnesium oxide to magnesium sulfate solutions yields crystalline oxysulfates at varying stoichiometric compositions, such as $\text{MgSO}_4 \cdot 3\text{MgO} \cdot 11\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 5\text{MgO} \cdot 8\text{H}_2\text{O}$.

Treatment of barium peroxide, BaO_2 with a concentrated solution of magnesium sulfate yields magnesium peroxide MgO_2 , a white powdery material used as a bleaching and oxidizing agent, and as an antacid in medicine.

Analysis

Elemental composition (of anhydrous MgSO_4) Mg 20.20%, S 26.63%, O 53.16%. The water of crystalization may be measured by thermogravimetric methods. Magnesium may be analyzed by AA or ICP-AES following acid digestion.

MANGANESE

[7439-96-5]

Symbol: Mn; atomic number 25; atomic weight 54.938; a Group VIIB (Group 7) transition metal; electron configuration $[\text{Ar}]4s^23d^5$; atomic radius 1.27Å; valence 0, +1, +2, +3, +4, +5, +6, +7; most common oxidation states +2, +4 and +7; stable natural isotope Mn-55 (100%)

History, Occurrence, and Uses

Manganese was recognized as an element by Scheele, Bergman and others in 1774 and isolated by Gahn in the same year. Gahn obtained the metal by thermal reduction of pyrolusite with carbon. The element derived its name from the Latin word, *magnes* which means magnet, referring to the magnetic properties of its ore pyrolusite.

Manganese is distributed widely in nature, mostly as oxide, silicate, and carbonate ores. Manganese ores often are found in association with iron ores in small quantities. The element, however, does not occur naturally in native form. Manganese is the twelfth most abundant element in the earth's crust.

Its concentration in the earth's crust is estimated to be 0.095%. Its average concentration in seawater is 2 μ g/L. Manganese also is found in large quantities in deep-sea nodules over the ocean floor at depths of 2.5 to 4 miles. The composition of some common manganese minerals is tabulated below:

Mineral	CAS Registry Number	Composition
Pyrolusite	[14854-26-3]	MnO ₂
Manganite	[52019-58-6]	Mn ₂ O ₃ · H ₂ O
Hausmannite	[1309-55-3]	Mn ₃ O ₄
Rhodochrosite	[598-62-9]	MnCO ₃
Rhodonite	[14567-57-8]	MnSiO ₃
Bementite	[66733-93-5]	Mn ₈ Si ₆ O ₁₅ (OH) ₁₀
Braunite	— — —	3Mn ₂ O ₃ · MnSiO ₃
Psilomelane	[12322-95-1]	BaMn ^{II} Mn ^{IV} ₈ O ₁₆ (OH) ₄

Manganese is used widely in industry: the most important use is in ferrous metallurgy. It also is used in chemical, electrochemical, food and pharmaceutical applications. Ferromanganese alloys are used in steel manufacturing. Manganese serves as a deoxidizer of molten steel and controls its sulfur content. Manganese metal also enhances strength and hardness of the alloy, and its resistance to corrosion. Manganese is used in high-temperature steels, stainless steels, manganese steel and various nickel-chromium and manganese-aluminum alloys. Practically all aluminum and magnesium alloys contain manganese.

Manganese is an essential element for plants and animals. Its shortage in soil can cause chlorosis or lack of chlorophyll in plants—manifested by the appearance of yellow or grey streaks on the leaves or mottling. It activates certain plant enzymes, such as *oxalosuccinic decarboxylase* in the oxidation of carbohydrates. Manganese deficiency can cause deformity of bones in animals.

In chemical industries, manganese is used to prepare several compounds. It also is used as a catalyst. Its salts have numerous applications in oxidation, catalysis, and medicine.

Physical Properties

Reddish-gray metal; exists in four allotropic modifications: alpha-, beta-, gamma- and delta forms. Alpha form has cubic crystal structure; 58 atoms per unit cell; density 7.43 g/cm³; brittle; transforms to beta form at 720°C. Beta-manganese is brittle and has a cubic lattice structure; containing 20 atoms per unit cube; transforms to gamma form at 1,100°C or back to alpha form on cooling; density 7.29 g/cm³. The gamma form exists as face-centered cubic crystal containing 4 atoms per unit cell; density 7.18 g/cm³; converts to delta form at 1,136°C. Delta-manganese consists of body-centered cubic crystals containing 2 atoms per unit cube; density 6.30 g/cm³; stable up to 1,244°C above which it melts to liquid.

Manganese vaporizes at 2,097°C; vapor pressure 0.9 torr at 1,244°C; hardness 5.0 (Mohs scale); magnetic susceptibility 9.9 cgs units at 18°C; electrical

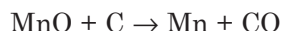
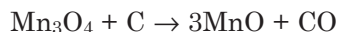
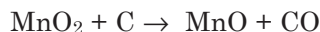
resistivities 185, 44, and 60 microhm-cm at 20°C for alpha-, beta- and gamma allotropes respectively; thermal neutron absorption 13.2 barns.

Thermochemical Properties

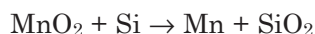
ΔH_f° (Mn-alpha)	0.0 kcal/mol
ΔH_f° (Mn-gamma)	0.37 kcal/mol
ΔH_f° (Mn-gas)	67.1 kcal/mol
ΔG_f° (Mn-alpha)	0.0 kcal/mol
ΔG_f° (Mn-gamma)	0.34 kcal/mol
ΔG_f° (Mn-gas)	57.0 kcal/mol
S° (Mn-alpha)	7.65 cal/degree mol
S° (Mn-beta)	8.22 cal/degree mol
S° (Mn-gamma)	7.75 cal/degree mol
S° (Mn-gas)	41.49 cal/degree mol
C_p (Mn-alpha)	6.29 cal/degree mol
C_p (Mn-beta)	6.34 cal/degree mol
C_p (Mn-gamma)	6.59 cal/degree mol
C_p (Mn-gas)	4.97 cal/degree mol
ΔH_{fus}	3.516 kcal/mol
Coefficient of linear expansion (at 25°C)	$22 \times 10^{-6}/^\circ\text{C}$

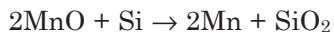
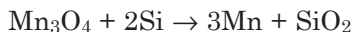
Production

Manganese is recovered primarily from its oxide ores, the most important being pyrolusite, MnO_2 . The basic method of producing the metal has not changed much since Gahn first isolated it by reducing manganese dioxide with carbon. Several processes to produce manganese meet its high demand in ferrous metallurgy. The oxides are reduced thermally in an electric furnace or a blast furnace. The ore is smelted at high temperatures in the presence of carbon, which reduces higher oxides of manganese, MnO_2 , Mn_2O_3 , and Mn_3O_4 into MnO , and then forms metallic manganese which has a relatively high vapor pressure:



Selection of the process depends on the requirement of the product, such as high-carbon or low-carbon ferromanganese or silicomanganese of varying carbon contents. Usually coke is used as a reducing agent for high-carbon ferromanganese for the steel industry. Low-carbon ferromanganese, silicomanganese, or refined ferromanganese that has low carbon content ranging from 0.1 to 1.5% maximum carbon, may be obtained by using silicon as a reducing agent:





Often, the manganese ores contain several other naturally occurring metal oxides such as alumina, silica, magnesia, and lime. Some of these oxides may be blended into manganese ore as fluxes to the furnace charge.

Manganese may be produced by electrolytic processes. Aqueous solutions of manganese(II) sulfate are used as the electrolyte. Mn ore is roasted and reduced with carbon or silicon to convert the higher oxides of manganese into MnO. The products are then leached with dilute sulfuric acid at pH 3. MnO dissolves in the acid forming manganese(II) sulfate. The solution is filtered and separated from insoluble residues. It then is neutralized with ammonia to pH 6–7.

Iron and aluminum precipitate out when treated with ammonia and are removed by filtration. Other metals, such as copper, zinc, lead and arsenic are precipitated and removed as sulfides upon passing hydrogen sulfide through the solution. Colloidal particles of metallic sulfides and sulfur are removed by treatment with iron(II) sulfide. The purified solution of manganese(II) sulfate is then electrolyzed in an electrolytic cell using lead anode and Hastelloy or Type 316 stainless steel cathode, both of which are resistant to acid. Manganese is deposited on the cathode as a thin film.

Manganese also is produced by electrolysis of fused salt. In one such process, the reduced MnO is blended to molten calcium fluoride and lime. The latter is used to neutralize silica in the ore. The fused composition of these salts is electrolyzed at 1,300°C in an electrolytic cell made up of high temperature ceramic material, using a carbon anode and a cathode consisting of iron bars internally cooled by water.

Reactions

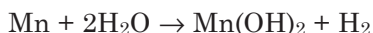
Manganese forms compounds in several valence states: 0, +1, +2, +3, +4, +5, +6, and +7. Of these, the valences 0, +1, and +5 are very uncommon. The divalent salts are the most stable. While in the divalent state, the metal is a reducing agent; in tetravalent state it is an oxidizing agent. Heptavalent manganese (Mn^{7+}) is a powerful oxidizing agent. Some examples of Mn compounds in all these oxidation states are tabulated below:

Oxidation State	Example
Mn(0)	$\text{Mn}_2(\text{CO})_{10}$
Mn(I)	$\text{C}_9\text{H}_7\text{Mn}(\text{CO})_3$
Mn(II)	MnCl_2 ; MnSO_4 ; MnO
Mn(III)	MnF_3 ; Mn_2O_3
Mn(IV)	MnO_2 ; K_2MnO_3
Mn(V)	K_3MnO_4
Mn(VI)	K_2MnO_4 ; BaMnO_4
Mn(VII)	KMnO_4 ; Mn_2O_7

Many chemical properties of manganese are similar to iron. Manganese burns in air or oxygen at elevated temperatures forming trimanganese tetroxide:

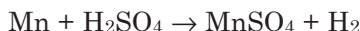
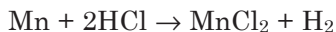


The metal reacts slowly with water in cold, forming manganous hydroxide with the evolution of hydrogen:

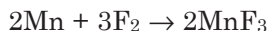
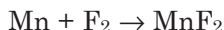
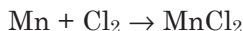


The reaction is usually slow below 100°C, but proceeds rapidly upon heating.

Manganese reacts readily with dilute mineral acids forming their divalent salts and liberating hydrogen:



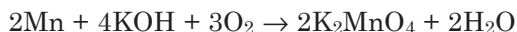
Manganese forms manganese(II) halides when heated with halogens. With fluorine, reaction is very vigorous and the products are MnF_2 and MnF_3 :



When heated with sulfur, the product is manganese(II) sulfide, MnS_2 .

Manganese combines with carbon or silicon at elevated temperatures forming a series of carbides or silicides having compositions such as Mn_2C_7 , Mn_3C , Mn_7C_3 and Mn_{15}C_4 or MnSi , Mn_3Si and Mn_5Si_3 . Manganese reacts with nitrogen above 750°C forming various nitrides, such as Mn_3N_2 , Mn_5N_2 and Mn_4N . The metal ignites in nitrogen at 1,200°C, then burns with a heavy, smoky flame forming the above nitrides. The principal product is Mn_3N_2 . Also reaction with anhydrous ammonia above 350°C yields several nitrides of varying composition.

Manganese dissolves in concentrated alkali in boiling solutions forming manganese(II) hydroxide and hydrogen. However, in the presence of excess oxygen or under oxygen pressure, the product is a manganate:



Reactions with concentrated acids are slow at room temperature, but rapid when heated. No hydrogen forms in concentrated acids. With concentrated sulfuric and nitric acids, sulfur dioxide and nitric oxide form:





Manganese combines with several metals at elevated temperatures forming binary compounds in varying compositions. Such metals include Al, Zn, Ni, Sn, As, Sb, Be, Pd, and Au.

Analysis

Manganese in aqueous solution may be analyzed by several instrumental techniques including flame and furnace AA, ICP, ICP-MS, x-ray fluorescence and neutron activation. For atomic absorption and emission spectrometric determination the measurement may be done at the wavelengths 279.5, 257.61 or 294.92 nm respectively. The metal or its insoluble compounds must be digested with nitric acid alone or in combination with another acid. Soluble salts may be dissolved in water and the aqueous solution analyzed. X-ray methods may be applied for non-destructive determination of the metal. The detection limits in these methods are higher than those obtained by the AA or ICP methods. ICP-MS is the most sensitive technique. Several colorimetric methods also are known, but such measurements require that the manganese salts be aqueous. These methods are susceptible to interference.

Manganese produces violet color in an oxidizing flame on a microcosmic or borax bead. The color disappears in a reducing flame.

Toxicity

Although trace amounts of manganese are essential for animals, in large quantities the metal can cause acute and chronic poisoning. Chronic inhalation of metal dust or fumes can cause manganism, a nonfatal disease affecting the central nervous system. The symptoms are mental disorder and disturbance in speech.

MANGANESE(II) CARBONATE

[598-62-9]

Formula: MnCO_3 ; MW 114.95

Synonyms: manganous carbonate; manganese spar; rhodochrosite

Occurrence and Uses

Manganese(II) carbonate occurs in nature as the mineral rhodochrosite [14476-12-1] (manganese spar). This ore also is used to produce manganese dioxide (by electrolytic process). The pure compound is used as gemstones; and as a pigment (manganese white).

Physical Properties

Pinkish-red translucent crystals; hexagonal-rhombohedral structure; refractive index 1.597; density 3.70 g/cm³; hardness 3.8 Mohs; decomposes above 200°C; slightly soluble in water; $K_{\text{sp}} 2.24 \times 10^{-11}$; soluble in dilute acids.

Thermochemical Properties

ΔH_f° (cry)	-214.0 kcal/mol
ΔH_f° (ppt)	-210.9 kcal/mol
ΔG_f° (cry)	-195.9 kcal/mol
ΔG_f° (ppt)	-194.0 kcal/mol
S° (cry)	20.5 cal/degree mol
S° (ppt)	27.0 cal/degree mol

Preparation

Manganese(II) carbonate is mined from its naturally occurring mineral rhodochrosite. The compound may be prepared in the laboratory as a pale-pink precipitate by adding sodium bicarbonate to a solution of manganese(II) salt saturated with carbon dioxide. The product obtained is monohydrate, $\text{MnCO}_3 \cdot \text{H}_2\text{O}$. However, if the carbon dioxide-saturated solution, together with the above monohydrate precipitate, is heated in the absence of atmosphere oxygen, the monohydrate $\text{MnCO}_3 \cdot \text{H}_2\text{O}$ is converted into the anhydrous MnCO_3 .

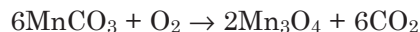
Reactions

The dry carbonate decomposes on heating, forming manganese(II) oxide and CO_2 :

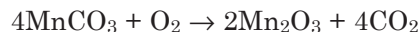


When heated above 330°C , MnO is partially oxidized by CO_2 , thus the decomposition products also contain MnO_2 and CO .

When heated in air, the carbonate yields Mn_3O_4 :



When heated in oxygen, manganese(III) oxide forms:



Reaction with dilute acids forms manganese salts of the acids, liberating CO_2 :

**Analysis**

Elemental composition: Mn 47.79%, C 10.45%, O 41.76%. The compound is dissolved in dilute HCl and CO_2 liberated is identified by the lime water test (turns lime water milky), by GC-TCD, or GC/MS. The characteristic mass for CO_2 is 44. The acid solution may be analyzed for Mn by AA, ICP or other instrumental technique (see Manganese).

MANGANESE(II) CHLORIDE

[7773-01-5]

Formula: MnCl_2 ; MW 125.84; forms a stable tetrahydrate, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$

Synonyms: manganous chloride; manganese dichloride; scacchite

Uses

Manganese(II) chloride is used in dyeing and printing textiles and as a disinfectant. It also is used in dry cell batteries; for the preparation of drying agents for paints and varnishes; as a catalyst in chlorination reactions; in the production of several manganese salts, including methylcyclopentadienyl-manganese tricarbonyl used as a colorant for brick. In metallurgy, the compound is used as an alloying agent and is added to molten magnesium to produce magnesium-manganese alloys.

Physical Properties

The anhydrous chloride is a pink solid; cubic crystals; deliquescent; density 2.977 g/cm^3 at 25°C ; melts at 650°C ; vaporizes at $1,190^\circ\text{C}$; very soluble in water ($\sim 72 \text{ g/100 mL}$ at 25°C); soluble in alcohol; insoluble in ether.

The tetrahydrate has a rose color; monoclinic crystal structure; deliquescent; density 2.01 g/cm^3 ; melts at 58°C ; loses one molecule of water at 106°C and all water at 198°C ; highly soluble in water (151 g/100 mL at 8°C) and extremely soluble in boiling water (656 g/100 mL at 100°C); soluble in ethanol; insoluble in ether.

Thermochemical Properties

$\Delta H_f^\circ (\text{MnCl}_2)$	-115.0 kcal/mol
$\Delta H_f^\circ (\text{MnCl}_2 \cdot 4\text{H}_2\text{O})$	-403.3 kcal/mol
$\Delta G_f^\circ (\text{MnCl}_2)$	-105.3 kcal/mol
$\Delta G_f^\circ (\text{MnCl}_2 \cdot 4\text{H}_2\text{O})$	-340.3 kcal/mol
$S^\circ (\text{MnCl}_2)$	$28.26 \text{ cal/degree mol}$
$S^\circ \text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	$72.5 \text{ cal/degree mol}$
$C_p (\text{MnCl}_2)$	$17.43 \text{ cal/degree mol}$

Preparation

Manganese(II) chloride is prepared by heating manganese(II) oxide, manganese dioxide, manganese(II) carbonate or manganese(II) hydroxide with hydrochloric acid:



When the product mixture is evaporated below 58°C , the tetrahydrate salt, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ is obtained.

Manganese(II) chloride is a by-product in the manufacture of chlorine from manganese dioxide and hydrochloric acid (the Weldon process).

Anhydrous chloride can be prepared by heating manganese(II) oxide or manganese(II) carbonate with dry hydrogen chloride; or by burning the metal in chlorine at 700°C to 1,000°C.

The anhydrous salt can also be obtained by slowly heating the tetrahydrate, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in a rotary drier above 200°C or by dehydration in a stream of hydrogen chloride gas.

Reactions

Manganese(II) chloride forms double salts with alkali metal chlorides when mixed in stoichiometric amounts. Such double salts, which can decompose in water, may have compositions like KMnCl_3 or K_2MnCl_4 .

Manganese(II) chloride forms adducts with ammonia, hydroxylamine and many other nitrogen compounds. Many adducts are stable at ordinary temperatures. Examples are $\text{MnCl}_2 \cdot 6\text{NH}_3$ and $\text{MnCl}_2 \cdot 2\text{NH}_2\text{OH}$.

An aqueous solution can readily undergo double decomposition reactions with soluble salts of other metals, producing precipitates of insoluble salts of Mn(II) or other metals.

Analysis

Elemental composition: Mn 43.66%, Cl 56.34%

An aqueous solution of the compound may be analyzed for Mn by AA, ICP, or other instrumental techniques, and for chloride by ion chromatography or titration against a standard solution of silver or mercuric nitrate.

MANGANESE DECACARBONYL

[10170-69-1]

Formula: $\text{Mn}_2(\text{CO})_{10}$; MW 389.99; manganese in zero oxidation state.

Synonyms: dimanganese decacarbonyl; manganese carbonyl

Uses

Manganese decacarbonyl is used as an antiknock additive to gasoline; and as a catalyst.

Physical Properties

Golden-yellow monoclinic crystals; density 1.75 g/cm³; melts at 154 to 155°C; decomposition commences around 110°C, slowly losing carbon monoxide; stable under carbon monoxide atmosphere; insoluble in water; soluble in most organic solvents.

Preparation

Manganese decacarbonyl is prepared by the reduction of methylcyclopentadienylmanganese tricarbonyl (MMT) with sodium in diglyme under carbon monoxide pressure.

Alternatively, the compound can be prepared by reduction of manganese(II) iodide with a Grignard reagent in the presence of carbon monoxide under pressure.

Analysis

Elemental composition: Mn 28.17%, C 30.80%, O 41.03%. The compound is cautiously digested with nitric acid, diluted and analyzed for manganese by instrumental techniques. Its solution in an organic solvent may be analyzed by GC/MS.

Toxicity

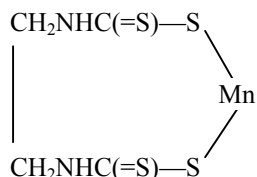
The compound is toxic by ingestion and possibly by other routes of exposure.

MANGANESE ETHYLENEBIS(THIOCARBAMATE)

[12427-38-2]

Formula: $C_4H_6MnN_2S_4$; MW 256.29

Structure:



Synonyms: Maneb; [ethylenebis(dithiocarbamato)]manganese; manganous ethylenebis(dithiocarbamate)

Uses

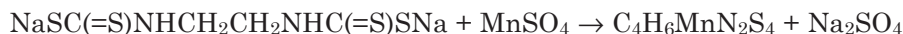
The compound is a fungicide.

Physical Properties

Yellow powder; crystallizes from methanol or ethanol; melts between 192° to 204°C; low solubility in water; soluble in chloroform and pyridine.

Preparation

Manganese ethylenebis(thiocarbamate) is made by adding disodium ethylenebis(dithiocarbamate) (also, known as Nabam, commercially available) to an aqueous solution of manganese(II) sulfate:



Alternatively, the compound may be prepared by neutralizing an aqueous solution of disodiummethylenbis(dithiocarbamate) (Nabam) with acetic acid followed by addition of manganese(II) chloride solution.

Analysis

Elemental composition: Mn 20.70%, S 48.35%, C 18.11%, N 10.56%, H 2.28%. A chloroform solution of the compound may be analyzed by GC/MS or by GC-FPD. Manganese may be determined by digesting the compound with nitric acid and analyzing the diluted acid extract by AA or ICP.

Toxicity

Maneb is toxic by ingestion.

MANGANESE(II) HYDROXIDE

[18933-05-6]

Formula: $\text{Mn}(\text{OH})_2$; MW 88.953

Synonyms: manganous hydroxide; pyrochroite

Occurrence: Manganese(II) hydroxide occurs naturally as the mineral pyrochroite

Physical Properties

Pink hexagonal crystal; density 3.26 g/cm³; refractive index 1.68; Mohs hardness 2.5; decomposes at 140°C; insoluble in water; K_{sp} 5.61×10^{-12} ; soluble in acid; dissolves in alkaline solution on heating.

Thermochemical Properties

ΔH_f°	-167.0 kcal/mol
ΔG_f°	-148.0 kcal/mol
S°	23.0 cal/degree mol

Preparation

Manganese(II) hydroxide is obtained as a white precipitate by adding a solution of sodium or potassium hydroxide to a solution of manganese(II) salt, such as manganese(II) chloride:



The white precipitate rapidly turns brownish-pink in air. The reaction does not occur with ammonia in the presence of ammonium salt.

The hydroxide also is found in nature as mineral pyrochroite in the form of white transparent leaflets. The white leaflets turn pink on exposure to air.

Reactions

Manganese(II) hydroxide is a base exhibiting weak amphoteric behavior. It reacts with acids forming the corresponding manganese(II) salt:



The hydroxide is rapidly oxidized in air forming manganese(III) oxide, Mn_2O_3 .

Analysis

Elemental composition: Mn 61.76%, H 2.27%, O 35.97%. The compound is digested in nitric acid and analyzed for manganese by AA, ICP or other instrumental technique.

MANGANESE(II) OXIDE

[1344-43-0]

Formula: MnO ; MW 70.94

Synonyms: manganous oxide; manganese monoxide; green manganese oxide; manganosite [1313-12-8]

Occurrence and Uses

Manganese(II) oxide occurs naturally as manganosite [1313-12-8]. The mineral is found very rarely in nature. Manganese(II) oxide is used in the fertilizer industry as a source of manganese in fertilizers; in feedstuff formulations; and as an intermediate in the production of several manganese compounds.

Physical Properties

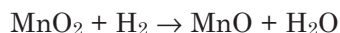
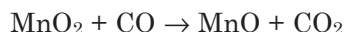
Green cubic crystal; refractive index 2.16; density 5.37 g/cm³ at 23°C; Moh's hardness 5.5; melts at 1945°C; insoluble in water.

Thermochemical Properties

ΔH_f°	-92.07 kcal/mol
ΔG_f°	-86.74 kcal/mol
S°	14.27 cal/degree mol
C_p	10.86 cal/degree mol

Production

Manganese(II) oxide is obtained commercially from manganese(IV) oxide (manganese dioxide) by the reduction with hydrogen, carbon monoxide or methane at elevated temperatures (>800°C):



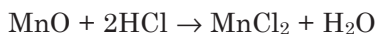
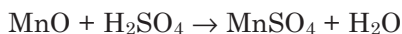
The oxide also can be made by thermal decomposition of manganese(II) carbonate or manganese(II) oxalate in the absence of air:



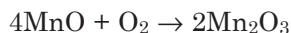
Also, careful dehydration of manganese(II) hydroxide, $\text{Mn}(\text{OH})_2$, under controlled conditions in the absence of air yields MnO .

Reactions

Manganese(II) oxide is the lowest oxide of manganese and it is purely a basic oxide. It reacts with acids to form their manganese(II) salts:



The compound also is oxidized by air or oxygen to higher oxides of manganese. When heated cautiously in air, the product is manganese sesquioxide or manganese(III) oxide:

**Analysis**

Elemental composition: Mn 77.44%, O 22.55%. The oxide can be characterized nondestructively by x-ray methods. Also, manganese may be analyzed by AA or ICP technique following acid digestion with nitric acid and diluting the acid extract appropriately (see Manganese).

MANGANESE(III) OXIDE

[1317-34-6]

Formula: Mn_2O_3 ; MW 157.87

Synonyms: manganese sesquioxide; dimanganese trioxide

Occurrence and Uses

Manganese(III) oxide occurs in nature as the mineral braunite. The oxide is used in the production of ferrites and thermistors.

Physical Properties

Black cubic (or rhombic) crystals; density 4.50 g/cm³; Moh's hardness 6–6.5 (for braunite); decomposes at about 875°C; insoluble in water; insoluble in alcohol and acetone; soluble in acids.

Thermochemical Properties

ΔH_f°	–229.2 kcal/mol
ΔG_f°	–210.6 kcal/mol
S°	26.40 cal/degree mol
C_p	25.73 cal/degree mol

Preparation

Manganese(III) oxide is obtained by heating manganese(II) oxide in air at 600 to 850°C. It also may be prepared by igniting manganese(II) salts in air

or oxygen. The oxide also is produced by cautious heating of manganese(II) oxide in oxygen. Manganese(III) oxide also can be made by dehydrating manganese(III) metahydroxide, $\text{MnO}(\text{OH})$, in a vacuum at 250°C . In such preparation, an unstable tetragonal modification, $\beta\text{-Mn}_2\text{O}_3$, is first obtained which on prolonged heating converts to the stable cubic modification, $\alpha\text{-Mn}_2\text{O}_3$.

Analysis

Elemental composition: Mn 69.59%, O 30.41%. The oxide can be characterized by x-ray methods and analyzed for manganese by AA or ICP following acid extraction.

MANGANESE(II,III) OXIDE

[1317-35-7]

Formula: Mn_3O_4 ; MW 228.81

Synonyms: trimanganese tetraoxide; manganomanganic oxide; red oxide of manganese

Occurrence and Use

Manganese(II,III) oxide occurs in nature as the mineral hausmannite [1309-55-3]. It is used to make ferrites and thermistors. The oxide also is used in the thermite process for producing manganese.

Physical Properties

Black tetragonal crystal; exhibits two allotropic modifications—a stable α phase, occurring in tetragonal crystalline form (as hausmannite) and an unstable β modification; density 4.85 g/cm^3 ; Moh's hardness 5.5; melts at $1,567^\circ\text{C}$; insoluble in water; soluble in hydrochloric acid.

Thermochemical Properties

ΔH_f°	-331.7 kcal/mol
ΔG_f°	-306.7 kcal/mol
S°	$37.2 \text{ cal/degree mol}$
C_p	$33.4 \text{ cal/degree mol}$

Preparation

Manganese(II,III) oxide is made by heating manganese(IV) oxide, MnO_2 , or manganese(III) oxide, Mn_2O_3 , above 950°C . When Mn_2O_3 is heated in air, the temperature should be above 940°C , but if heated in oxygen, the temperature should be above $1,090^\circ\text{C}$. Also, heating manganese(III) oxide at 230°C in hydrogen yields Mn_3O_4 . However, further heating above 300°C converts Mn_3O_4 formed to green manganese(II) oxide, MnO .

Manganese(II,III) oxide also is obtained by heating the dioxide, MnO_2 , with carbon at 600 to 700°C .

Reactions

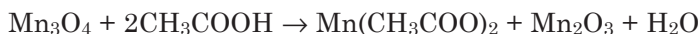
Manganese(II,III) oxide reacts with dilute acids forming the corresponding manganous salt and manganese(IV) oxide, MnO_2 :



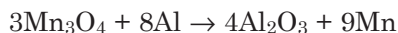
The oxide, however, dissolves slowly in cold sulfuric acid forming a red solution that also contains manganic sulfate, $\text{Mn}_2(\text{SO}_4)_3$:



Reaction with acetic acid yields manganese(II) acetate and manganese(III) oxide:



Manganese(II,III) oxide is reduced to manganese metal when heated with powdered aluminum (the Thermite process). The reaction is vigorous and exothermic:

**Analysis**

Elemental composition: Mn 72.03%, O 27.98%. The oxide can be characterized by x-ray methods. Manganese in the oxide can be analyzed by AA or ICP method after digesting the oxide in nitric acid.

MANGANESE(IV) OXIDE

[1313-13-9]

Formula: MnO_2 ; MW 86.937

Synonyms: manganese dioxide; manganese peroxide; black manganese oxide

Occurrence and Uses

Manganese(IV) oxide is the most important ore of manganese from which the metal is mostly manufactured. The oxide occurs in nature as the mineral pyrolusite as heavy gray lumps, or black when powdered.

The mineral is used to produce manganese metal, most manganese salts, and also manganese steel and other alloys. The metallurgical applications of manganese(IV) oxide mainly involve making ferromanganese and special manganese alloys. Another important application of manganese(IV) oxide is in manufacturing dry-cell batteries and alkaline cells. The oxide also is a colorant in brick, tile, porcelain and glass; a drier for paints and varnishes; a

preparation for printing and dyeing textiles; a curing agent for polysulfide rubbers; an adsorbent for hydrogen sulfide and sulfur dioxide; an oxidizing agent in many organic syntheses such as quinone and hydroquinone; and a catalyst in laboratory preparation of oxygen from potassium chlorate. Manganese(IV) oxide also is used to make welding rods and fluxes, and ceramic magnets (ferrites); and is an additive to fertilizers.

Physical Properties

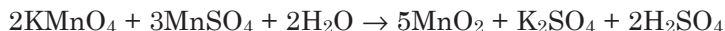
Black tetragonal crystals; density 5.08 g/cm³; Moh's hardness 6.3; decomposes at 535°C; insoluble in water.

Thermochemical Properties

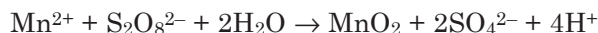
ΔH_f°	-124.3 kcal/mol
ΔG_f°	-111.2 kcal/mol
S°	12.69 cal/degree mol
C_p	12.93 cal/degree mol

Preparation

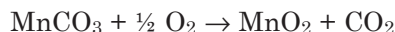
Pure manganese(IV) oxide (precipitate form) may be prepared by reducing permanganate ion with a manganous salt:



Manganese(IV) oxide can also be precipitated by oxidation of a manganese(II) salt using an oxidizing agent such as hypochlorite or peroxydisulfate:



Manganese(IV) oxide may also be made by thermal decomposition of manganese(II) nitrate; or from roasting manganese(II) carbonate in air:



A highly active gamma-MnO₂ can be produced by treating manganese(III) oxide with hot sulfuric acid:



Mn₂O₃ is derived from pyrolusite by heating the mineral at 600–800°C or reducing with powdered coal at 300°C.

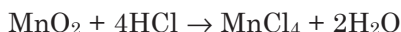
Reactions

Thermal decomposition of manganese(IV) oxide at 600 to 800°C yields manganese(III) oxide:



MnO_2 also is reduced to Mn_2O_3 at 300°C in the presence of a reducing agent such as hydrogen, methane or carbon.

Treatment with concentrated hydrochloric acid forms manganese(IV) chloride which readily decomposes to manganese(III) chloride and manganese(II) chloride, successively liberating chlorine:



When heated with concentrated sulfuric acid, manganese(IV) oxide yields manganese(II) sulfate, evolving oxygen:



When the solution is heated at 135°C , MnSO_4 is oxidized to $\text{Mn}_2(\text{SO}_4)_3$. Reaction with sulfuric acid in the presence of oxalic acid yields manganese(II) sulfate and carbon dioxide:



While the reaction with sulfuric acid in the presence of sodium chloride evolves chlorine:



When heated with potassium hydroxide, manganese(IV) oxide partially decomposes to manganese(III) oxide and potassium manganate:



However, in the presence of oxygen or other oxidizing agents, all manganese is oxidized to manganate:

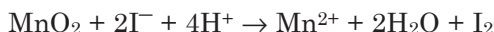


Manganate(VI) can further oxidize to manganate(VII) (or permanganate) in alkaline solution with a strong oxidizing agent such as hypochlorite, chlorine or perchlorate, or under anodic oxidation. Alternatively, in less alkaline media (where the KOH concentration is less than about 15%), the manganate ion MnO_4^{2-} hydrolyzes, disproportionating to permanganate MnO_4^- and forming back manganese(IV) oxide:

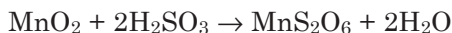


The green color of manganate solution turns purple due to the permanganate formed.

Manganese(IV) oxide is an oxidizing agent. In acid medium, it oxidizes iodide to iodine:



Thus, in the presence of dilute acids, MnO_2 is readily attacked by strong reducing agents. Similarly, reaction with sulfurous acid forms manganese(II) dithionate:



Or with nitrous acid in the presence of nitric acid, manganese(II) nitrate is formed:



Reaction with potassium bifluoride in the presence of hydrofluoric acid creates a stable complex fluoride, K_2MnF_6 in which Mn is in +4 oxidation state:



When fused with basic oxides such as calcium oxide, manganites or manganate(IV) salts such as $\text{CaO} \cdot \text{MnO}_2$, $2\text{CaO} \cdot \text{MnO}_2$, $\text{CaO} \cdot 3\text{MnO}_2$ are formed. The stoichiometric compositions of these manganites vary.

Manganese(IV) oxide reacts with aniline in the presence of sulfuric acid forming quinone, an intermediate product in the manufacture of hydroquinone:



Analysis

Elemental composition: Mn 63.19%, O 36.81%. The pure oxide may be characterized by x-ray crystallography. The MnO_2 content in pyrolusite may be measured by titration. An excess of a standard solution of oxalic acid is added to a solution of MnO_2 in sulfuric acid. After all solid MnO_2 dissolves, the excess oxalic acid is measured by titrating against a standard solution of potassium permanganate (see Reactions).

Alternatively, pyrolusite is heated with concentrated hydrochloric acid and

the chlorine evolved is passed through a solution of potassium iodide. The iodine liberated is titrated against a standard solution of sodium thiosulfate using starch indicator. One mol MnO_2 is equivalent to two mol thiosulfate. Also, acid extracts of MnO_2 may be diluted and measured by AA or ICP techniques (See Manganese).

MANGANESE(II) SULFATE

[7785-87-7]

Formula: MnSO_4 ; MW 151.00; forms stable monohydrate, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ [10034-96-5] and tetrahydrate, $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ [10101-68-5]

Synonym: manganous sulfate

Uses

Manganese(II) sulfate is used to produce manganese by an electrolytic process. The compound is used for dyeing textiles; for producing red glazes on porcelain; in varnish driers; in fertilizers; and in animal feeds to provide manganese as an essential trace element.

Physical Properties

The anhydrous salt is a white orthogonal crystal; density 3.25 g/cm^3 ; melts at 700°C ; decomposes at 850°C ; very soluble in water.

The monohydrate $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ consists of red monoclinic crystals; density 2.95 g/cm^3 ; highly soluble in water. The tetrahydrate $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ is a pink solid; monoclinic crystals; density 2.107 g/cm^3 ; highly soluble in water; more soluble than the anhydrous salt or the monohydrate.

Thermochemical Properties

$\Delta H_f^\circ (\text{MnSO}_4)$	-254.60 kcal/mol
$\Delta H_f^\circ (\text{MnSO}_4 \cdot \text{H}_2\text{O})$	-329.00 kcal/mol
$\Delta H_f^\circ (\text{MnSO}_4 \cdot 4\text{H}_2\text{O})$	-539.70 kcal/mol
$\Delta G_f^\circ (\text{MnSO}_4)$	-228.83 kcal/mol
$S^\circ (\text{MnSO}_4)$	$26.8 \text{ cal/degree mol}$
$C_p (\text{MnSO}_4)$	$24.0 \text{ cal/degree mol}$

Preparation

Manganese(II) sulfate is prepared by prolonged heating of any manganese salt with concentrated sulfuric acid. The compound is produced commercially from pyrolusite (MnO_2) or rhodochrosite (MnCO_3). Either mineral is dissolved in sulfuric acid and the solution evaporated:



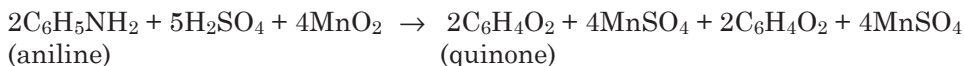
Alternatively, manganese dioxide is heated strongly with dehydrated iron(II)

sulfate:



Manganese(II) sulfate, prepared by methods involving evaporation of manganese salt with sulfuric acid, is the tetrahydrate, $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$. The tetrahydrate on gentle heating produces monohydrate, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$.

Also, manganese(II) sulfate is a by-product in the manufacture of hydroquinone. The process involves reaction of aniline with manganese dioxide in sulfuric acid, followed by the removal of quinone by steam distillation under vacuum.



The unreacted acid is neutralized by lime, treated with water, and the solution filtered to separate any excess MnO_2 and insoluble residues. Evaporation of the filtrate yields a crude product containing about 80% MnSO_4 and 15% $(\text{NH}_4)_2\text{SO}_4$.

Manganese(II) sulfate also may be produced by the action of sulfur dioxide with manganese dioxide:



Reactions

Aqueous solution of manganese(II) sulfate undergoes double decomposition reactions precipitating insoluble manganese(II) salts; for example, adding caustic soda solution precipitates manganese(II) hydroxide.

Manganese(II) sulfate forms several double salts, such as manganese(II) ammonium sulfate, $(\text{NH}_4)_2\text{Mn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.

Reaction with oxalic acid, stearic acid, phthalic acid or their alkali salts yield their corresponding manganese salts (manganese soaps).

Manganese(II) sulfate may be oxidized electrolytically to manganese dioxide (gamma form) in an electrolytic cell.



Manganous(II) sulfate is a reducing agent. Treatment with oxidizing agents can yield manganese compounds in a higher oxidation state.

Analysis

Elemental composition: Mn 36.38%, S 21.23%, O 42.38%. Manganese may be analyzed in an aqueous solution of the compound by AA, ICP or x-ray fluorescence methods. Sulfate can be determined by ion chromatography. Water of crystallization in hydrated sulfate may be measured by heating at 400°C (by gravimetry).